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M.S. Chouhan
Solution Manual
Advanced Problems in
Organic Chemistry
for JEE
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in Organic Chemistry
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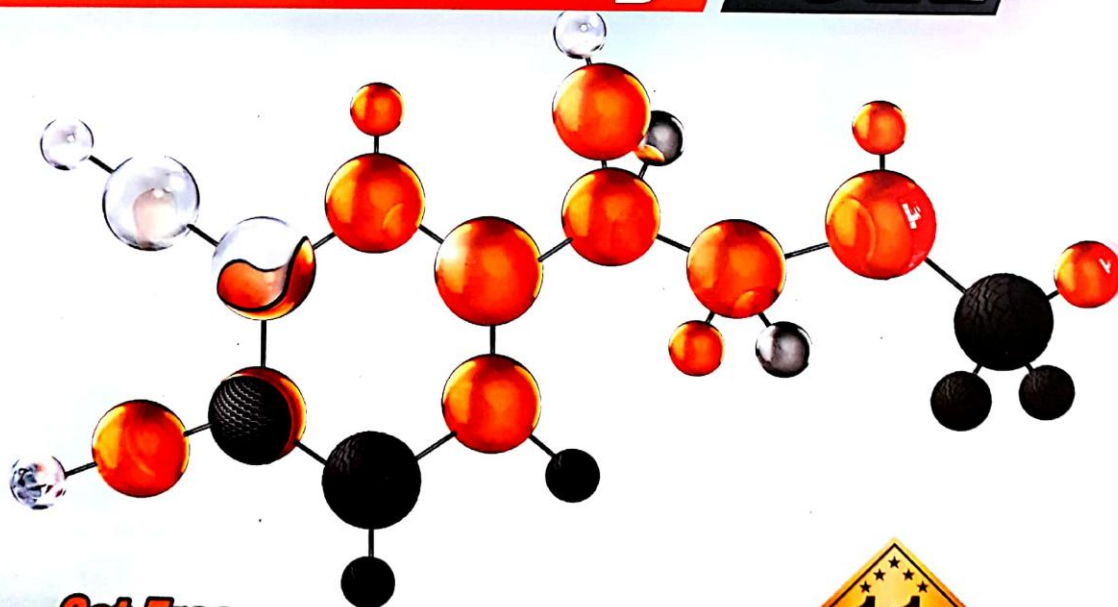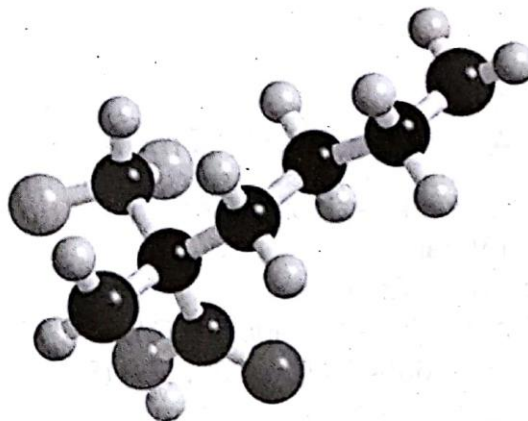
Solution Manual

Advanced Problems *in* ORGANIC CHEMISTRY *for* JEE

by :

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CONTENTS

About the Author

Mahendra Singh Chouhan (MSC Sir) is a renowned name in the realm of Organic Chemistry. Through a Chemical Engineer from Mumbai University, his great passion for the subject led him to impart guidance to IIT-JEE aspirants on a regular basis. His in depth knowledge and vast experience has helped innumerable students to achieve their dream of excelling at IIT, JEE and other such tough challenges.

He has launched a website to extend the benefits of his expertise beyond the geographical barriers to all those who dare to dream and seek - www.iitjeeorganic.com.

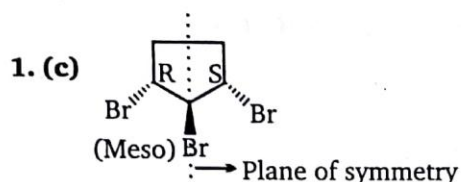
The website provides expert guidance in all the areas of the subject in a most skillful manner. There are quizzes, challenging questions, notes, e-books and videos etc. This website is a complete guide in itself for organic chemistry and has been designed for IIT-JEE aspirants, keeping in mind the various syllabi and CBSE.

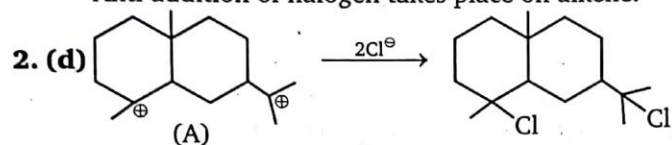
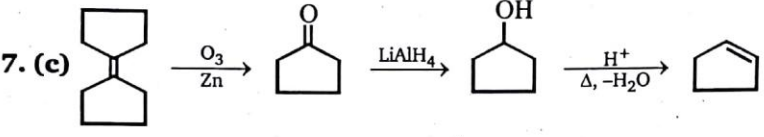
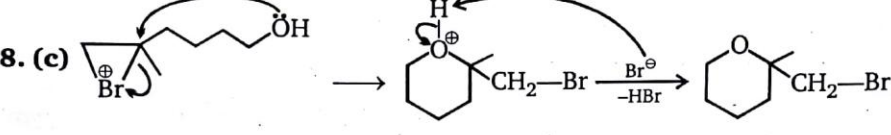
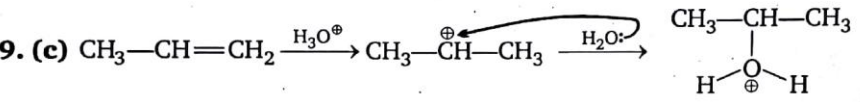
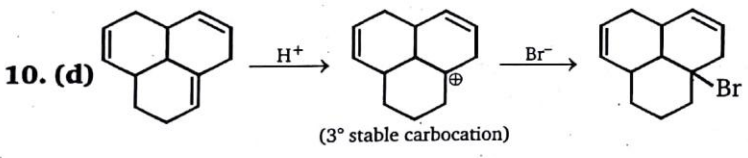
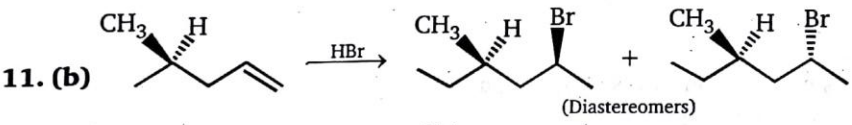
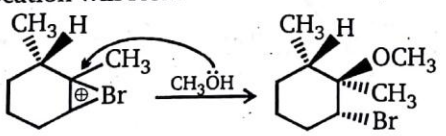
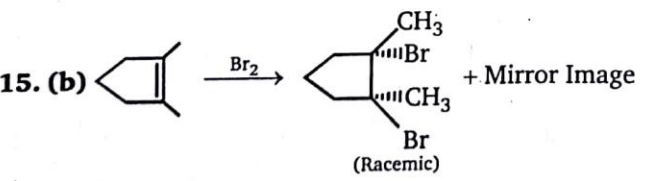
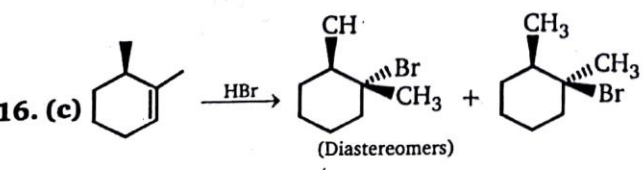
Highly recommended for the high flyers.

4(B) Hydrocarbons (Alkenes)

Level-1

1. (c) (Meso) Br

⋮ → Plane of symmetry

Anti addition of halogen takes place on alkene.

2. (d) (A) Carbocation $\xrightarrow{2Cl^{\ominus}}$

Source of this carbocation can be (a), (b) and (c).

3. (c) Ring expansion take place.

$\xrightarrow{H-Cl}$ $\xrightarrow{\text{Ring expansion}}$ $\xrightarrow{Cl^{\ominus}}$

4. (d) ⟷ (o-xylene) Which on ozonolysis give a, b and c.

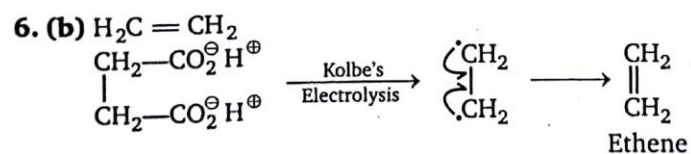
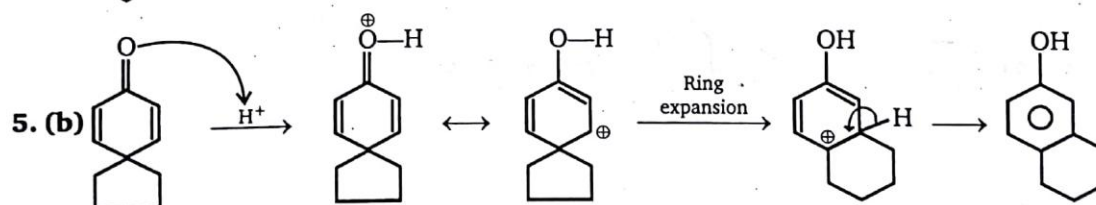
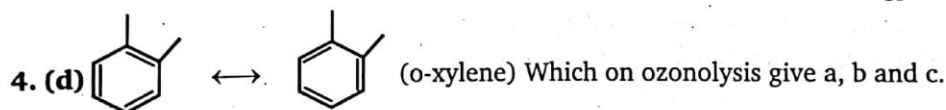
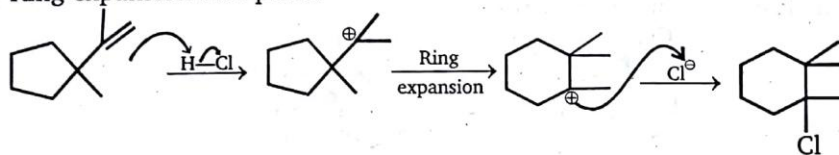
5. (b) $\xrightarrow{H^+}$ ⟷ $\xrightarrow{\text{Ring expansion}}$ ⟶

6. (b) $H_2C = CH_2$

$$\begin{array}{l} CH_2-CO_2^{\ominus}H^{\oplus} \\ | \\ CH_2-CO_2^{\ominus}H^{\oplus} \end{array} \xrightarrow[\text{Electrolysis}]{\text{Kolbe's}} \begin{array}{l} \dot{C}H_2 \\ | \\ \dot{C}H_2 \end{array} \longrightarrow \begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array}$$

Ethene

7. (c) $\xrightarrow[Zn]{O_3}$ O $\xrightarrow{LiAlH_4}$ OH $\xrightarrow[\Delta, -H_2O]{H^+}$

8. (c) $\ddot{O}H$, $\overset{\oplus}{Br}$ $\longrightarrow$ H, $\overset{\oplus}{O}$, $CH_2—Br$ $\xrightarrow[-HBr]{Br^{\ominus}}$ O, $CH_2—Br$

9. (c) $CH_3—CH{=}CH_2 \xrightarrow{H_3O^{\oplus}} CH_3—\overset{\oplus}{C}H—CH_3 \xrightarrow{H_2\ddot{O}:}$ $CH_3—CH—CH_3$ with $H—\overset{\oplus}{O}—H$

10. (d) $\xrightarrow{H^+}$ ⊕ (3° stable carbocation) $\xrightarrow{Br^-}$ Br

11. (b) CH_3, H $\xrightarrow{HBr}$ CH_3, H, Br + CH_3, H, Br (Diastereomers)

12. (d) Non-classical carbocation will form

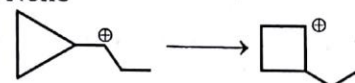
CH_3, H, CH_3, ⊕Br $\xrightarrow{CH_3\ddot{O}H}$ CH_3, H, OCH_3, CH_3, Br

13. (c) Because of formation of new chiral center.

14. (b) Transition state = Intermediate +1

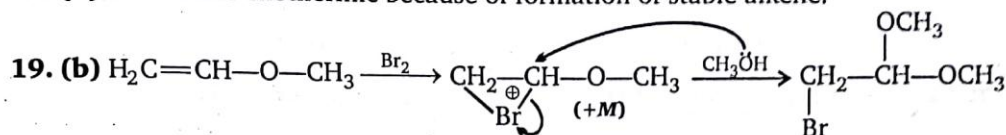
15. (b) $\xrightarrow{Br_2}$ CH_3, Br, CH_3, Br + Mirror Image (Racemic)

16. (c) $\xrightarrow{HBr}$ CH, Br, CH_3 + CH_3, CH_3, Br (Diastereomers)

17. (d) None

(cyclopropyl carbocation) ⟶ (cyclobutyl carbocation) This carbocation rearrangement is not favourable.

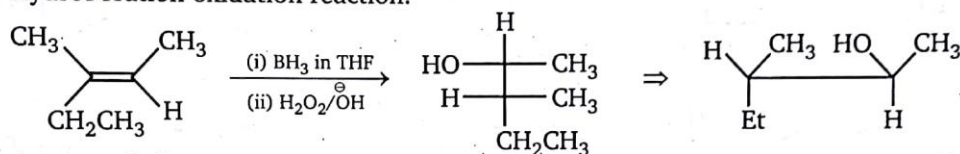
(σ-resonance stabilized)

18. (d) Reaction is exothermic because of formation of stable alkene.

19. (b) $H_2C{=}CH{-}O{-}CH_3 \xrightarrow{Br_2} CH_2{-}\overset{\oplus}{CH}{-}O{-}CH_3$ (bromonium, $+M$) $\xrightarrow{CH_3\ddot{O}H} CH_2(Br){-}CH(OCH_3){-}OCH_3$

20. (d) 1,2 and 1,4- addition take place.

21. (b) NBS + aq. DMSO is used for preparation of halohydrin.

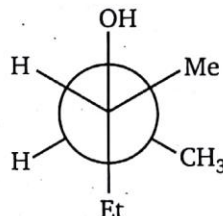
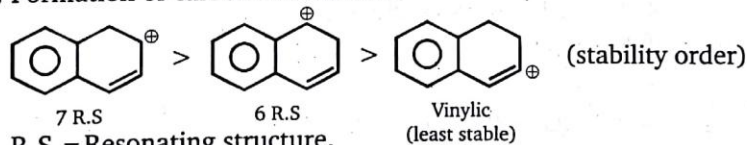
22. (b) Hydroboration oxidation reaction.

(E)-3-methyl-2-pentene $\xrightarrow[\text{(ii) } H_2O_2/\overset{\ominus}{O}H]{\text{(i) } BH_3 \text{ in THF}}$ Fischer projection: H (top); HO—C—CH_3; H—C—CH_3; CH_2CH_3 (bottom) ⇒ H, CH_3, HO, CH_3, Et, H

Hydroboration oxidation is syn addition

(Newman projection: OH, H, Me, H, CH_3, Et)

23. (b) Formation of carbocation is r.d.s.

(7 R.S) > (6 R.S) > Vinylic (least stable) (stability order)

R. S. = Resonating structure.

24. (b) Two products will be obtained by addition reaction above and below the plane of ring. It is the example of syn hydroxylation.

25. (b) Intramolecular nucleophilic attack.

$H(H_3C)C{=}C{=}CH{-}C(CH_3)_2{-}CH_2{-}OH \xrightarrow[CCl_4]{Br_2}$ bromonium intermediate ($\overset{\oplus}{Br}$) with $-CH_2\ddot{O}H$ attack

6-Membered ring formation

(product: bromo-dihydropyran with H, H_3C, CH_3, CH_3, Br, O)

26. (b) $CH_3-C(CH_3)_2-H \xrightarrow{H-F} CH_3-\overset{\oplus}{C}(CH_3)_2 + H_2C=CH_2 \longrightarrow CH_3-C(CH_3)_2-CH_2-\overset{\oplus}{C}H_2$

1,2 $H^{\ominus}$ shift

$CH_3-C(CH_3)_2-\overset{\oplus}{C}H-CH_3 \xrightarrow{1,2,\ \overset{\ominus}{C}H_3 \text{ shift}} CH_3-\overset{\oplus}{C}(CH_3)-\underset{\alpha}{CH}(CH_3)-CH_3 \longrightarrow$ (tetramethylethylene)

27. (d) $\xrightarrow{H^+}$ (3° Carbocation stable) $\xrightarrow{\text{Ring expansion}}$ $\xrightarrow{1,2-\overset{\ominus}{C}H_3 \text{ shift}}$ $\longrightarrow$

28. (b) $\xrightarrow[\Delta]{H^+}$ $\overset{\oplus}{C}H_2$ $\xrightarrow{1,2,\overset{\ominus}{H} \text{ shift}}$ $\xrightarrow{1,2-\overset{\ominus}{H} \text{ shift}}$ $\longrightarrow$

(7α-H Major)

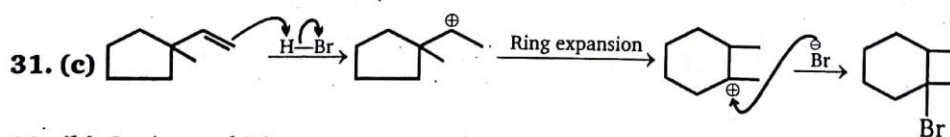
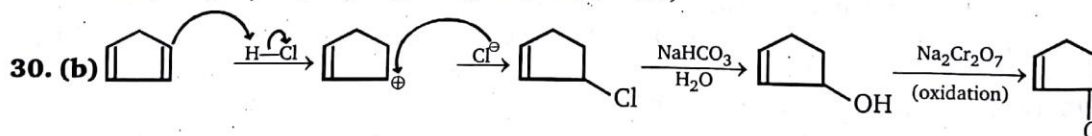
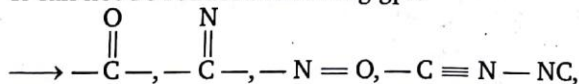
29. (d) Di-imide is used to reduce pi-bond formed between like atom.

For example $\longrightarrow -CH=CH-, -N=N-$

It can not be reduced following gps.

$\longrightarrow -\overset{O}{\overset{\|}{C}}-, -\overset{N}{\overset{\|}{C}}-, -N=O, -C\equiv N-NC,$

30. (b) $\xrightarrow{H-Cl}$ $\xrightarrow{Cl^{\ominus}}$ Cl $\xrightarrow[H_2O]{NaHCO_3}$ OH $\xrightarrow[\text{(oxidation)}]{Na_2Cr_2O_7}$ O

31. (c) $\xrightarrow{H-Br}$ $\xrightarrow{\text{Ring expansion}}$ $\xrightarrow{\overset{\ominus}{Br}}$ Br

32. (b) Conjugated Dienes on $KMnO_4/\Delta$ give oxalic acid.

33. (a) OH, H $\xrightarrow{OsO_4}$ OH, H H, OH OH H

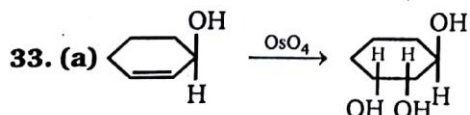
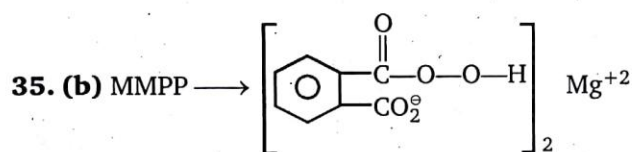
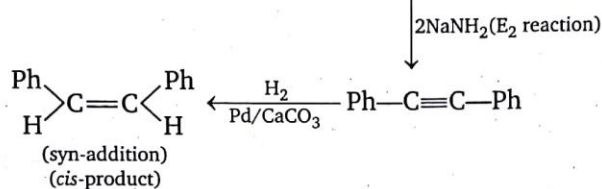
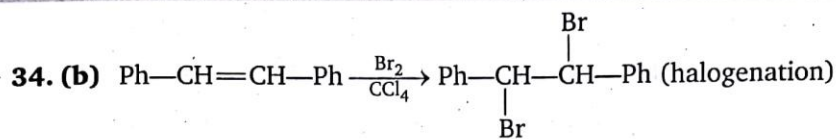
Because of less stric hinderance (a) is major

34. (b) Ph—CH=CH—Ph $\xrightarrow[CCl_4]{Br_2}$ Ph—CH(Br)—CH(Br)—Ph (halogenation)

$\downarrow$ $2NaNH_2$ (E_2 reaction)

Ph(H)C=C(H)Ph $\xleftarrow[Pd/CaCO_3]{H_2}$ Ph—C≡C—Ph

(syn-addition)
(*cis*-product)

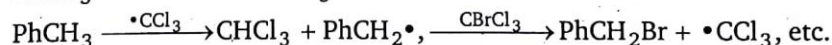
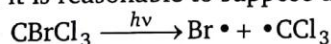
35. (b) MMPP $\longrightarrow$ $\left[C_6H_4(CO_2^{\ominus})\text{—}C(=O)\text{—}O\text{—}O\text{—}H \right]_2$ Mg^{+2}

will act as a electrophile so attack on that alkene which has more α-hydrogen or stable epoxide will formed, more substituted epoxide is more stable.

36. (b) More substituted alkene will undergo epoxide formation.

37. (b) Give compound on hydrolysis gives syn-acid.

38. (b) The use of light suggests a free radical mechanism. This means that the methane derivative will undergo homolytic fission. Since the C — Br bond is weaker than the C — Cl bond, it is reasonable to suppose that the former will be broken. Hence :

$$CBrCl_3 \xrightarrow{h\nu} Br\bullet + \bullet CCl_3$$

$$PhCH_3 \xrightarrow{\bullet CCl_3} CHCl_3 + PhCH_2\bullet, \xrightarrow{CBrCl_3} PhCH_2Br + \bullet CCl_3, \text{ etc.}$$

Attack by the free radical on toluene occurs at the methyl side - chain and not in the ring because the C — H bond in Me is weaker than that of a ring-hydrogen atom and the benzyl free radical is far more stable than an aryl free radical.

The other point that requires explanation is why toluene is attacked by the CCl_3 free radical and not by the bromine free radical. Activation energies involving free radicals are usually very low and so the controlling factor is the heat of reaction (or, more correctly, the free energy of reaction). The more exothermic the reaction (greater is ΔG), the more favoured is that reaction. If the bromine atom attacks, the result is HBr, the bond of which is much weaker than the C — H bond formed when $^\bullet CCl_3$ attacks. Hence, reaction proceeds by the later route.

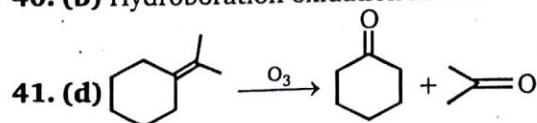
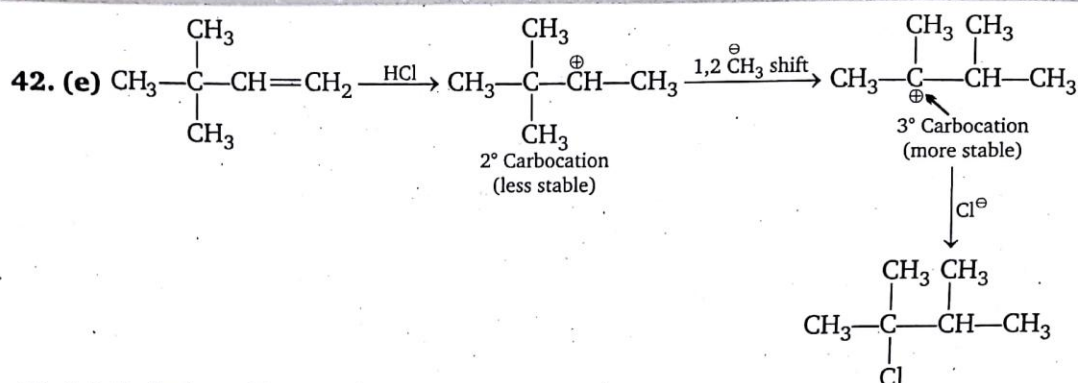
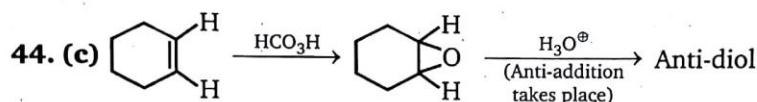
39. (b) More nucleophilic alkene will react.

40. (b) Hydroboration oxidation reaction.

41. (d) (cyclohexylidene)ethane $\xrightarrow{O_3}$ cyclohexanone + CH_3CHO

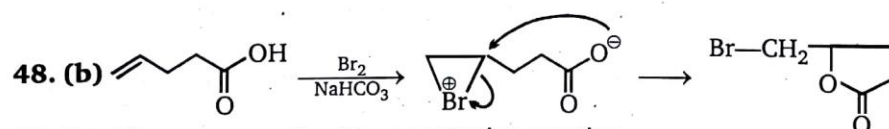
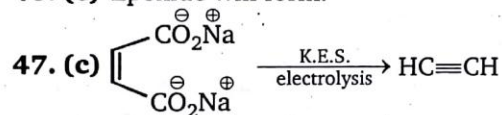
42. (e) $CH_3-C(CH_3)_2-CH=CH_2 \xrightarrow{HCl} CH_3-C(CH_3)_2-\overset{\oplus}{C}H-CH_3$ (2° Carbocation (less stable)) $\xrightarrow{1,2\ \overset{\ominus}{C}H_3\ \text{shift}} CH_3-\overset{\oplus}{C}(CH_3)-CH(CH_3)-CH_3$ (3° Carbocation (more stable)) $\xrightarrow{Cl^{\ominus}} CH_3-C(CH_3)(Cl)-CH(CH_3)-CH_3$

43. (c) Hydroboration – oxidation reaction.

44. (c) Cyclohexene $\xrightarrow{HCO_3H}$ epoxide $\xrightarrow[\text{(Anti-addition takes place)}]{H_3O^{\oplus}}$ Anti-diol

45. (a) Anti-addition take place.

46. (c) Epoxide will form.

47. (c) $\overset{\ominus}{C}O_2\overset{\oplus}{Na}-CH=CH-\overset{\ominus}{C}O_2\overset{\oplus}{Na} \xrightarrow[\text{electrolysis}]{\text{K.E.S.}} HC\equiv CH$

48. (b) $CH_2=CH-CH_2-CH_2-COOH \xrightarrow[NaHCO_3]{Br_2}$ bromonium ion (carboxylate attacks) $\longrightarrow$ Br—CH_2–lactone (γ-lactone)

49. (b) Alkoxymercuration-De-mercuration reaction.

50. (b) cis-diol will form (syn addition takes place)

51. (b) $Br_2/h\nu$ (low conc.) (or) N.B.S, Allylic free radical substitution reaction.

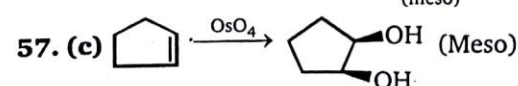
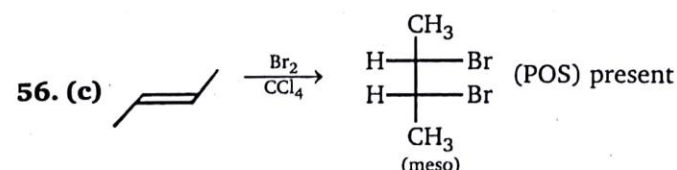
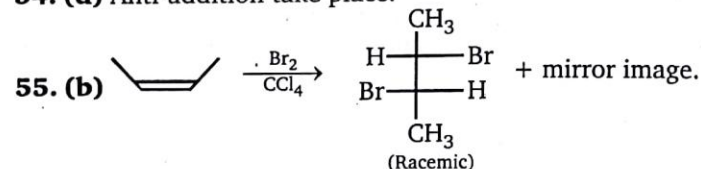
52. (a) Alkene will be cleaved by ozonolysis.

53. (b) cis-diol will form

54. (d) Anti-addition take place.

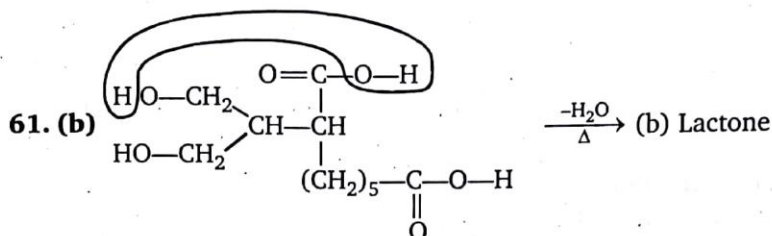
55. (b) cis-2-butene $\xrightarrow[CCl_4]{Br_2}$ Fischer projection: CH_3 (top); H–C–Br; Br–C–H; CH_3 (bottom) (Racemic) + mirror image.

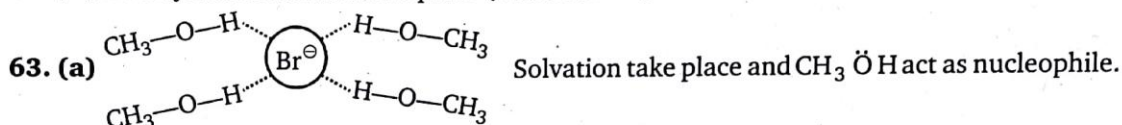
56. (c) trans-2-butene $\xrightarrow[CCl_4]{Br_2}$ Fischer projection: CH_3 (top); H–C–Br; H–C–Br; CH_3 (bottom) (meso) (POS) present

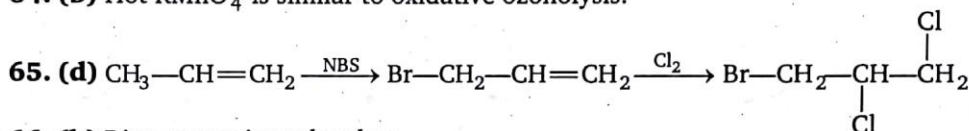
57. (c) Cyclopentene $\xrightarrow{OsO_4}$ cis-cyclopentane-1,2-diol (OH, OH) (Meso)

58. (b) Hydroboration - oxidation reaction is a syn-addition.

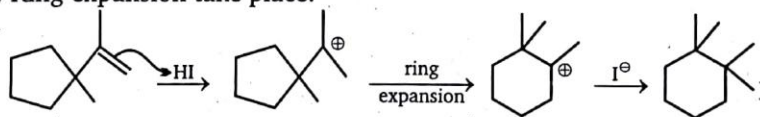
59. (c) Oxymercuration - Demercuration reaction addition of H_2O molecule is according to Markovnikoff's rule.

60. (a) Anti-Markovnikoff's addition take place (Peroxide effect operates).

61. (b) $(HO-CH_2)_2CH-CH(COOH)-(CH_2)_5-COOH \xrightarrow[\Delta]{-H_2O}$ (b) Lactone

62. (d) Halohydrin formation take place (anti-addition).

63. (a) $Br^{\ominus}$ solvated by four CH_3-O-H molecules. Solvation take place and $CH_3\ddot{O}H$ act as nucleophile.

64. (b) Hot $KMnO_4$ is similar to oxidative ozonolysis.

65. (d) $CH_3-CH=CH_2 \xrightarrow{NBS} Br-CH_2-CH=CH_2 \xrightarrow{Cl_2} Br-CH_2-CH(Cl)-CH_2Cl$

66. (b) Ring expansion take place.

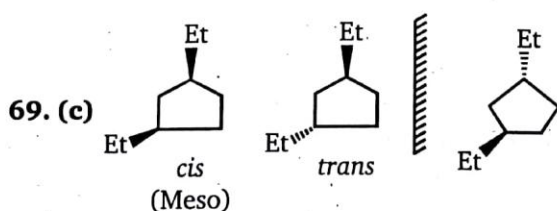
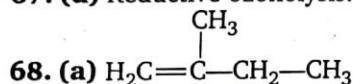
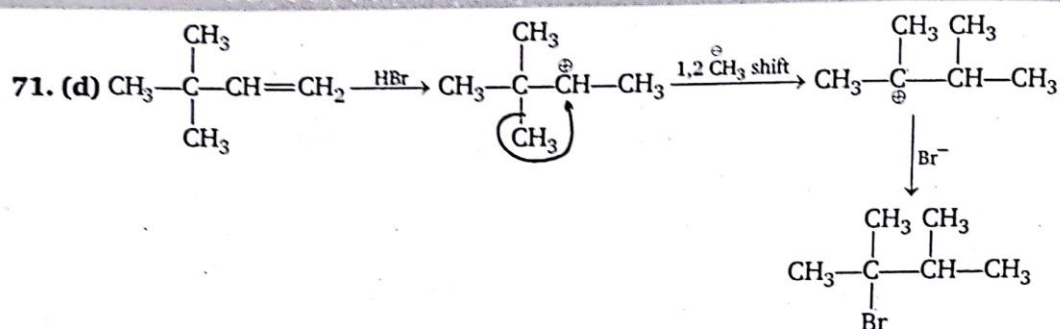
$\xrightarrow{HI}$ $\xrightarrow[\text{expansion}]{\text{ring}}$ $\xrightarrow{I^{\ominus}}$

67. (d) Reductive ozonolysis.

68. (a) $H_2C=C(CH_3)-CH_2-CH_3$

69. (c)

S. L = 3

70. (d) Markovnikoff's addition take place.

71. (d) $CH_3-C(CH_3)_2-CH=CH_2 \xrightarrow{HBr} CH_3-C(CH_3)_2-\overset{\oplus}{C}H-CH_3 \xrightarrow{1,2\ \overset{\ominus}{C}H_3\ \text{shift}} CH_3-\overset{\oplus}{C}(CH_3)-CH(CH_3)-CH_3 \xrightarrow{Br^-} CH_3-C(CH_3)(Br)-CH(CH_3)-CH_3$

72. (c) Hydroboration-oxidation reaction.

73. (d) Terminal alkyne will reacts with Tollen's reagent.

74. (c) Anti-Markovnikoff's addition take place.

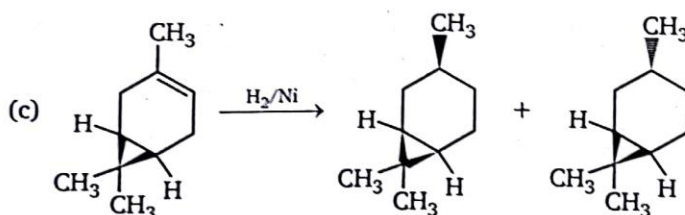
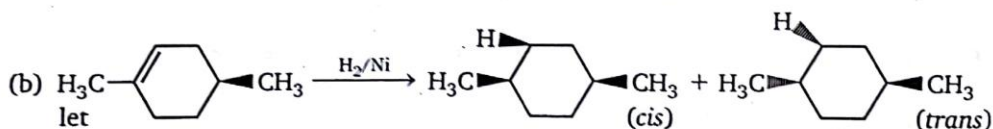
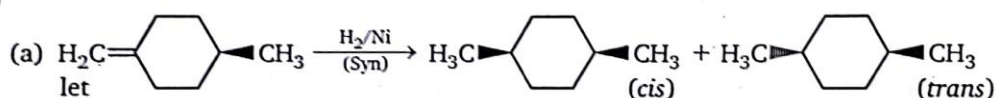
75. (a) Syn-addition take place.

76. (c) Reductive ozonolysis.

77. (d)

(a) $H_2C=$ (cyclohexylidene) $-CH_3$ (let) $\xrightarrow[(Syn)]{H_2/Ni}$ H_3C–cyclohexane–CH_3 (*cis*) + H_3C–cyclohexane–CH_3 (*trans*)

(b) H_3C–cyclohexene–CH_3 (let) $\xrightarrow{H_2/Ni}$ H_3C–cyclohexane(H)–CH_3 (*cis*) + H_3C–cyclohexane(H)–CH_3 (*trans*)

(c) bicyclic alkene (CH_3, H, CH_3, CH_3, H) $\xrightarrow{H_2/Ni}$ product (CH_3 up) + product (CH_3 down)

78. (b) Formation of carbocation is the rate determining step.

79. (d) Corresponding alkene is not possible.

80. (d) Non-classical carbocation will form.

81. (c) Attack of free radical on alkene is an propagation step.

82. (b) Attack of alkene take place of H — Cl.

83. (a) Carbocation formed will attacked by alkene.

84. (a) Hydroboration-oxidation take place (syn addition).

85. (a) Anti-addition take place.

(X) (erythro): COOH; H–C–Br; H–C–Br; COOH

(Y) (Threo): COOH; H–C–Br; Br–C–H; COOH

86. (d) (*P*) = [1-methoxy-4-methylcyclohexa-1,4-diene: ring with OCH_3 at top and CH_3 at bottom] More nucleophilic alkene will attack.

87. (b) Iodo lactonization.

88. (b) [cyclohexane ring bearing $\ddot{O}H$ and a $CH_2C(=CH_2)Cl$ side chain] $\xrightarrow{H^+}$ [carbocation with OH leaving] $\longrightarrow$ [bicyclic carbocation, $\oplus$–Cl] $\xrightarrow{H_2O}$ [bicyclic with $\ddot{O}H$ and Cl on same carbon] (unstable) $\downarrow$ [bicyclic ketone, =O]

89. (c) (*A*) $Ph—CH(Br)—CH_2—Br$ (*B*) $Ph—C\equiv C—H$ (*C*) $Ph—C\equiv C—CH_3$

90. (d) (a), (b) and (c) gives [1,4-dimethylcyclohexane, two stereoisomers with CH_3 at top and CH_3 at bottom] (cis & trans)

91. (b) [optically active dimethylcyclohexene] $\xrightarrow[Pt]{H_2}$ [meso dimethylcyclohexane] (POS) Present

optically active   meso

92. (b) [Fischer projection: Et top; Me–C*–H; Me–C*–Br; Et bottom] 4-Product

93. (a) [Fischer projection: CH_3 top; H–C–D; D–C–H; CH_3 bottom] + mirror image.

94. (a) $CH_3—CH_2—\overset{*}{C}H(Br)—CH_3$ (racemic mixture)

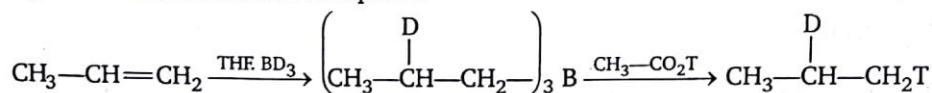
95. (a) Less steric hinderance site will be attacked. Approach of H_2 is more hindered in (b).

96. (d) Reductive ozonolysis.

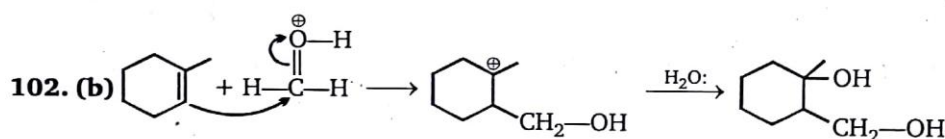
97. (b) Oxidation take place *i. e.*, epoxidation.

98. (a) Hydroboration-oxidation take place.

99. (c) Hydroboration-reduction take place.

$$CH_3-CH=CH_2 \xrightarrow{\text{THF. } BD_3} (CH_3-\underset{}{\overset{D}{CH}}-CH_2-)_3B \xrightarrow{CH_3-CO_2T} CH_3-\overset{D}{CH}-CH_2T$$

100. (d) $CH_3-CH_2-\underset{Cl}{CH}-CH=CH_2 \xrightarrow[Pt]{H_2} Et-\underset{Cl}{CH}-Et$ optically inactive.

101. (b) Cumulative dienes.

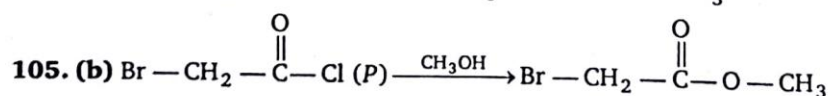
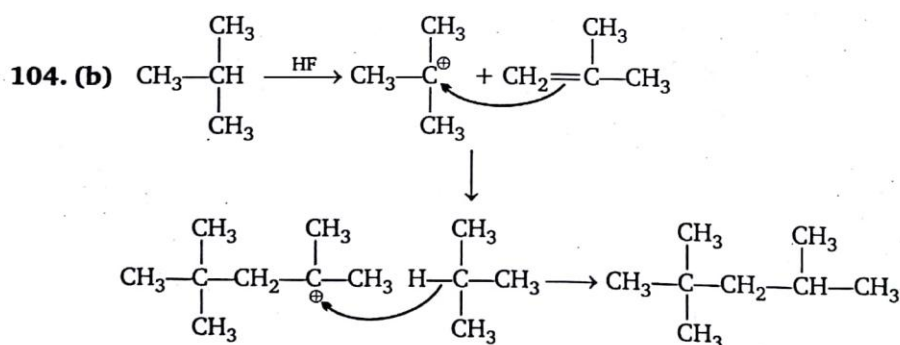
102. (b) 1-Methylcyclohexene $+ H-\overset{\oplus}{\overset{O-H}{\overset{\|}{C}}}-H \longrightarrow$ (tertiary carbocation, 2-CH_2-OH) $\xrightarrow{H_2O:}$ 1-methyl-2-(CH_2-OH)cyclohexan-1-ol (OH, CH_2-OH)

103. (d) (*A*) $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH$ (*B*) $CH_3-\overset{CH_3}{C}=CH_2$ (*C*) $CH_3-\overset{CH_3}{CH}-CH_2-Br$ (Anti-markovnikoff's addition take place)

104. (b) $CH_3-\underset{CH_3}{\overset{CH_3}{CH}} \xrightarrow{HF} CH_3-\underset{CH_3}{\overset{CH_3}{C^{\oplus}}} + CH_2=\overset{CH_3}{C}-CH_3$

$$\downarrow$$

$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\overset{CH_3}{\underset{\oplus}{C}}-CH_3 \quad H-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\overset{CH_3}{CH}-CH_3$$

105. (b) $Br-CH_2-\overset{O}{\overset{\|}{C}}-Cl\ (P) \xrightarrow{CH_3OH} Br-CH_2-\overset{O}{\overset{\|}{C}}-O-CH_3$

106. (c) (*A*) 1-methylcyclohexene (*B*) 1-methylcyclohexane-1,2-diol (OH, OH) (*C*) 2-hydroxy-2-methylcyclohexanone (OH, O)

107. (b) Markovnikoff's addition.

108. (b) Halohydrin will form (anti-addition).

109. (d) Hydroboration-oxidation take place.

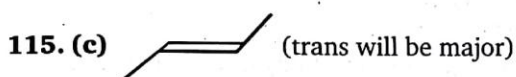
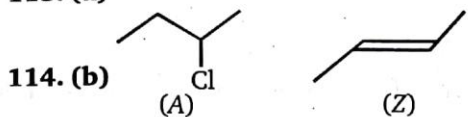
110. (d) Oxymercuration-Demercuration take place.
(Addition of —OH takes place according to Markovnikoff's Rule)

111. (c) Anti-addition take place. (*i.e.*, anti-hydroxylation)

112. (b)

113. (a)

114. (b) Cl (*A*) (*Z*)

115. (c) (trans will be major)

116. (a) *A* and *B* are diastereomers.

117. (b) Reduction followed by ozonolysis.

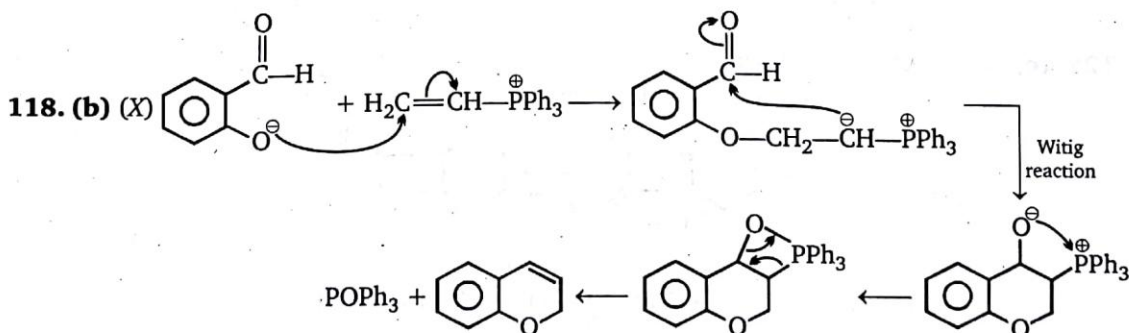
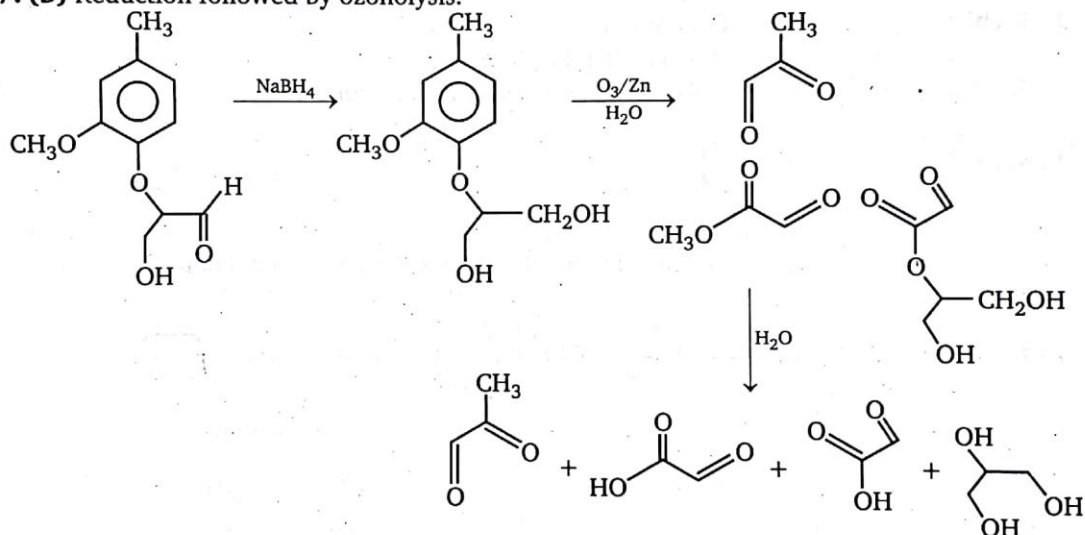
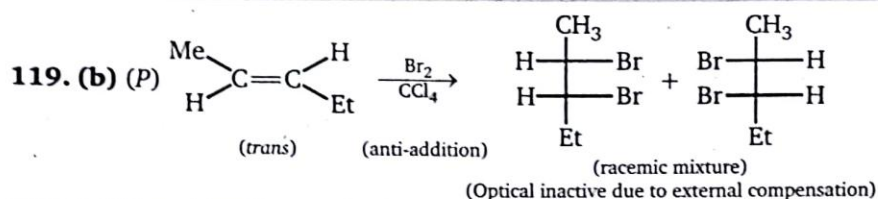
CH_3, CH_3O, O, H, O, OH $\xrightarrow{NaBH_4}$ CH_3, CH_3O, O, CH_2OH, OH $\xrightarrow[H_2O]{O_3/Zn}$ CH_3, O, O; O, CH_3O, O; O, O, O, CH_2OH, OH

$\downarrow H_2O$

CH_3, O, O + O, HO, O + O, O, OH + OH, OH, OH

118. (b) (*X*) O, C—H, $O^{\ominus}$ + $H_2C{=}CH{-}\overset{\oplus}{P}Ph_3$ ⟶ O, C—H, $O{-}CH_2{-}\overset{\ominus}{C}H{-}\overset{\oplus}{P}Ph_3$ $\xrightarrow{\text{Witig reaction}}$ $O^{\ominus}$, $\overset{\oplus}{P}Ph_3$, O ⟶ O, PPh_3, O ⟶ $POPh_3$ + O

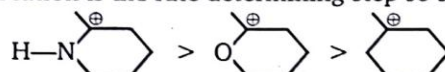
119. (b) (*P*) Me(H)C=C(H)Et (*trans*) $\xrightarrow[CCl_4]{Br_2}$ (anti-addition) CH_3–CH(H)(Br)–CH(H)(Br)–Et + CH_3–CH(Br)(H)–CH(Br)(H)–Et

(racemic mixture)
(Optical inactive due to external compensation)

120. (d) Unstable alkene will readily undergo reduction.

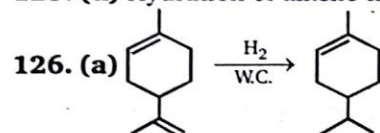
121. (b) (*B*) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-O-CH_3$. It is also obtained by reductive ozonolysis of $C(C_{11}H_{18}O_2)$.

122. (c) Oxidation of alkene followed by ozonolysis take place.

123. (a) Formation of carbocation is the rate determining step so stability of carbocation is.

H—N(ring)$^{\oplus}$ > O(ring)$^{\oplus}$ > (ring)$^{\oplus}$

124. (b) II ⟶ Markovnikoff's addition
III ⟶ Halogenation of alkane take place.

125. (d) Hydration of alkene take place. (Markonikov's addition)

126. (a) $\xrightarrow[W.C.]{H_2}$

less stable and less sterically hindered alkene will undergo reduction.

127. (b) Ph—C≡C—H $\xrightarrow{\overset{\ominus}{N}H_2}$ Ph—C≡$\overset{\ominus}{C}\overset{\oplus}{Na}$ + (cyclohexyl OTs) ⟶ Ph—C≡C—(cyclohexyl)

$\downarrow$ Na | liq. NH_3

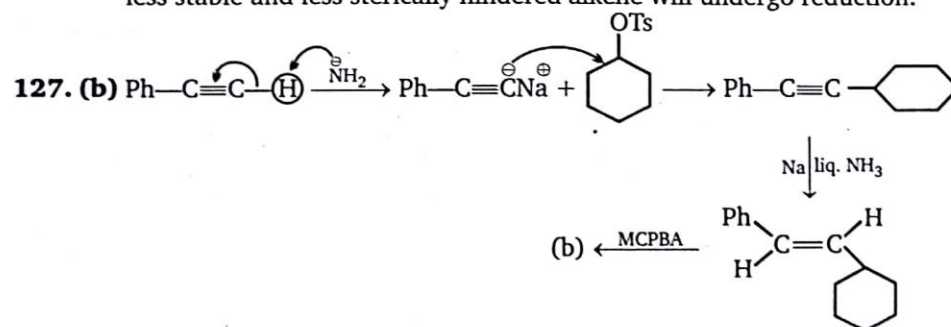
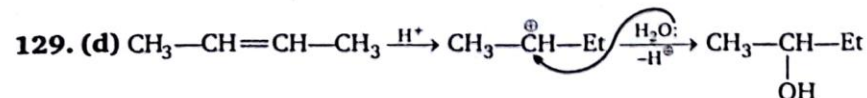
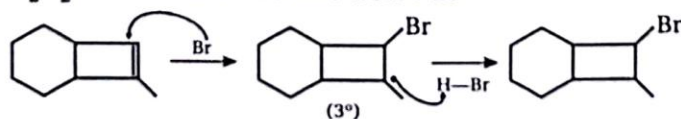
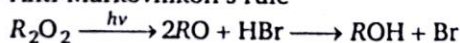
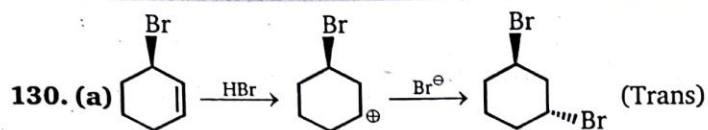
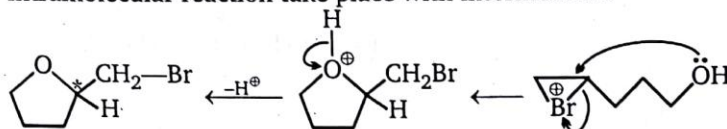
(b) $\xleftarrow{MCPBA}$ Ph(H)C=C(H)(cyclohexyl)

128. (c) Anti-Markovnikoff's rule

$R_2O_2 \xrightarrow{hv} 2RO + HBr \longrightarrow ROH + Br$

$\xrightarrow{Br}$ (3°) $\xrightarrow{H-Br}$

129. (d) $CH_3-CH=CH-CH_3 \xrightarrow{H^+} CH_3-\overset{\oplus}{C}H-Et \xrightarrow[-H^{\oplus}]{H_2O:} CH_3-\underset{OH}{\underset{|}{C}H}-Et$

130. (a) 3-bromocyclohexene $\xrightarrow{HBr}$ carbocation $\xrightarrow{Br^{\ominus}}$ 1,3-dibromocyclohexane (Trans)

131. (c) Intramolecular reaction take place with intermediate.

R and S configuration.

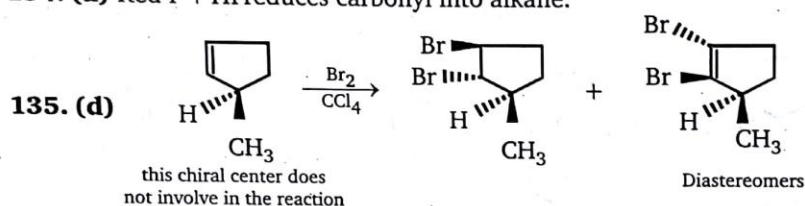
132. (d) More the stable carbocation more is rate.

133. (c) Aryl-halide is used.

$\therefore$ It is known as Wurtz fittig reaction.

134. (a) Red P + HI reduces carbonyl into alkane.

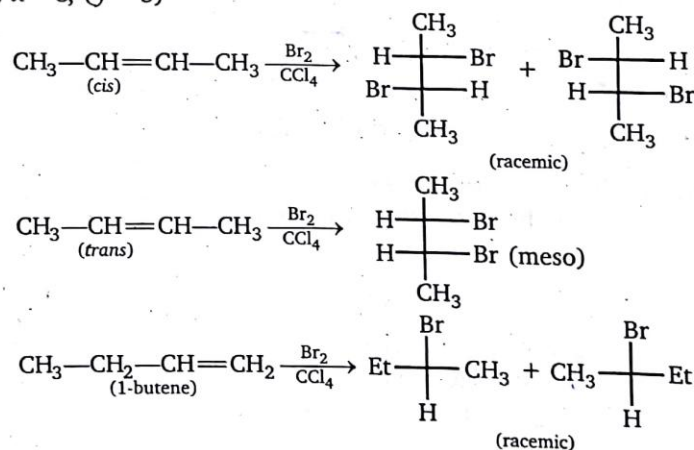
135. (d) $\xrightarrow[CCl_4]{Br_2}$ Diastereomers

this chiral center does not involve in the reaction

136. (c) $H-C\equiv C-H$ will precipitate and remaining gas will come out.

137. (b) $x = 3$, $(y = 5)$

$CH_3-CH=CH-CH_3$ (cis) $\xrightarrow[CCl_4]{Br_2}$ (racemic)

$CH_3-CH=CH-CH_3$ (trans) $\xrightarrow[CCl_4]{Br_2}$ (meso)

$CH_3-CH_2-CH=CH_2$ (1-butene) $\xrightarrow[CCl_4]{Br_2}$ Et–CHBr–CH_3 + CH_3–CHBr–Et (racemic)

138. (d) $H_2C=CH-\dot{C}H_2 > H_2C=\dot{C}H$

(resonance stabilized)

139. (d) Terminal alkene evolve CO_2 gas when treated with O_3/H_2O_2.

140. (b) a = Cold $KMnO_4$ (syn-addition)

b = $RCO_3H/H_3O^{\oplus}$ (anti-addition)

141. (b) $\xrightarrow[\text{Liq. NH}_3]{\text{Na}_3}$ (Birch reaction) $\xrightarrow[\text{Zn}]{\text{O}_3}$ $H-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-H + Ph_3P{=}CH_2$ (2 mole)

(Witting reaction)

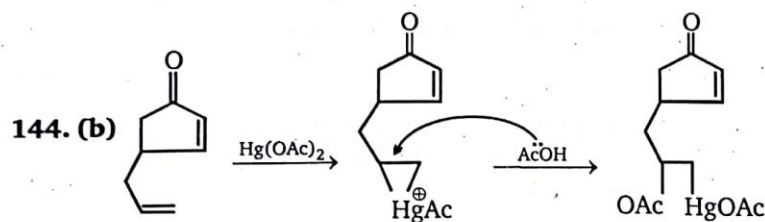
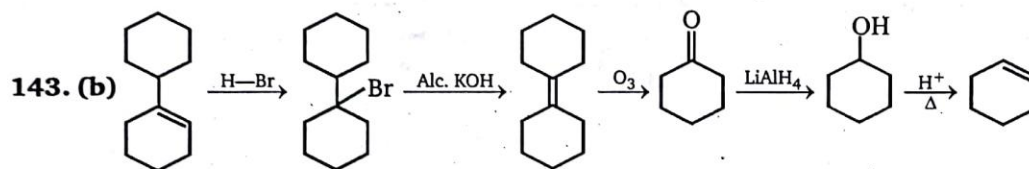
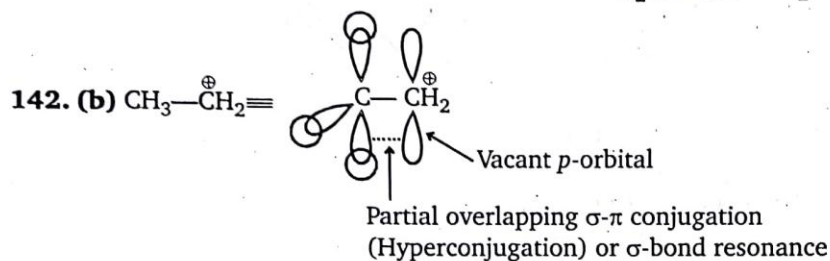
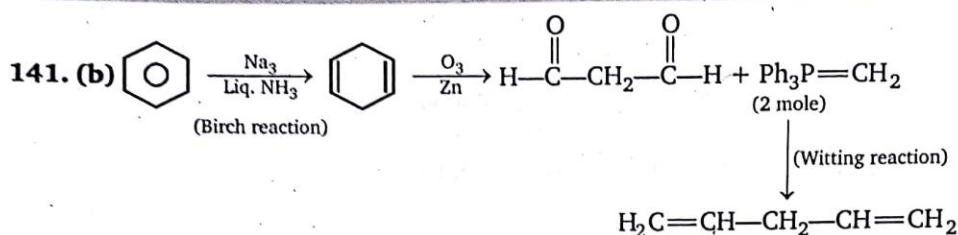
$H_2C{=}CH-CH_2-CH{=}CH_2$

142. (b) $CH_3-\overset{\oplus}{C}H_2 \equiv$ C— $\overset{\oplus}{C}H_2$

Vacant *p*-orbital

Partial overlapping σ-π conjugation (Hyperconjugation) or σ-bond resonance

143. (b) $\xrightarrow{\text{H—Br}}$ Br $\xrightarrow{\text{Alc. KOH}}$ $\xrightarrow{\text{O}_3}$ O $\xrightarrow{\text{LiAlH}_4}$ OH $\xrightarrow[\Delta]{\text{H}^+}$

144. (b) O $\xrightarrow{\text{Hg(OAc)}_2}$ $\overset{\oplus}{\text{Hg}}$Ac $\xrightarrow{\text{AcOH}}$ OAc HgOAc

145. (b) Most stable alkene less heat of hydrogenation.

a ⟶ 4α H Heat of hydrogenation → d > a > c > b

b ⟶ 10α H

c ⟶ 6α H

d ⟶ 3α H

146. (c) More the stable alkene less heat of hydrogenation.

a ⟶ 4α H Heat of hydrogenation

b ⟶ 2α H b > a > c > d

c ⟶ 5α H

d ⟶ 8α H

147. (b) $\overset{\oplus}{\text{Hg}}$ OAc O—H ⟶ O $\overset{\oplus}{\text{H}}$gOAc $\xrightarrow{\text{NaBH}_4}$ O

Above reaction is a intramolecular OMDM reaction.

148. (a) Cyclobutyl–C(CH_3)=CH_2 $\xrightarrow{H-Br}$ Cyclobutyl–$\overset{\oplus}{C}$(CH_3)–CH_3 $\xrightarrow{\text{Ring expension}}$ cyclopentyl cation (gem-dimethyl) $\xrightarrow{\text{1,2 methyl shift}}$ cation $\xrightarrow{Br^{\ominus}}$ Br-substituted dimethylcyclopentane

149. (d) 1-methylcyclopentene $\xrightarrow[CCl_4]{HBr}$ 1-methylcyclopentyl cation $\xrightarrow{Br^{\ominus}}$ 1-bromo-1-methylcyclopentane (Br)

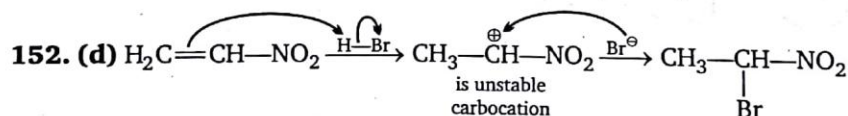
150. (b) $CH_3-\underset{}{\overset{CH_3}{\overset{|}{C}}}=CH-CH_3 \xrightarrow{\overset{\oplus}{H}gOAc} CH_3-\overset{CH_3}{\overset{|}{C}}-CH-CH_3$ (bridged $\overset{\ominus}{H}gOAc$) $\xrightarrow{EtOH} CH_3-\overset{CH_3}{\overset{|}{C}}-CH-CH_3$ (with OEt on C and HgOAc on CH)

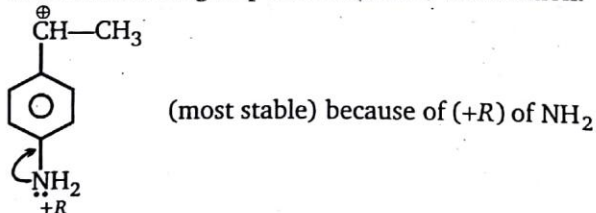
151. (a) $Me-\overset{Me}{\overset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-Me \xrightarrow[\Delta,\ 350°C]{Al_2O_3} Me-\overset{Me}{\overset{|}{C}}=CH-Me \xrightarrow{HI} Me-\overset{Me}{\overset{|}{\underset{I}{\underset{|}{C}}}}-CH_2-Me$

$AgI + Me-\overset{Me}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-CH_2-Me \xleftarrow[S_N1(\text{react.})]{AgOH}$

Al_2O_3 is dehydrating agent.

152. (d) $H_2C=CH-NO_2 \xrightarrow{H-Br} CH_3-\overset{\oplus}{C}H-NO_2 \xrightarrow{Br^{\ominus}} CH_3-\underset{Br}{\underset{|}{CH}}-NO_2$

is unstable carbocation

153. (c) Rate determining step is formation of carbocation.

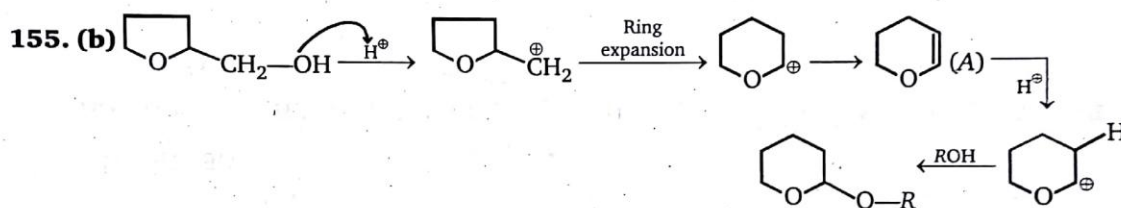
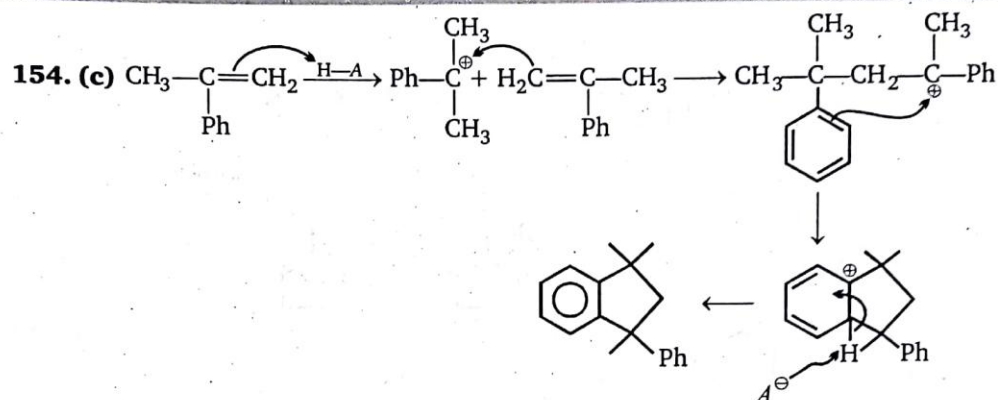
p-$H_2\ddot{N}$–C_6H_4–$\overset{\oplus}{C}H-CH_3$ (+R) (most stable) because of (+R) of NH_2

(a) is least stable due to (–R) of —NO_2

(b) +R (—OH)

(c) —CH_3 (hyperconjunction)

154. (c) $CH_3-C(Ph)=CH_2 \xrightarrow{H-A} Ph-\overset{\oplus}{C}(CH_3)_2 + H_2C=C(Ph)-CH_3 \longrightarrow CH_3-C(CH_3)(Ph)-CH_2-\overset{\oplus}{C}(CH_3)-Ph$

$A^{\ominus}$ H Ph

155. (b) $\xrightarrow{H^{\oplus}}$ $\overset{\oplus}{C}H_2$ $\xrightarrow{\text{Ring expansion}}$ (A) $H^{\oplus}$ ROH $O-R$

156. (c) Carbocation obtained by reaction (1) and (2) are resonating structure of each other.

157. (a) Low temperature kinetic control high temperature thermodynamic control.

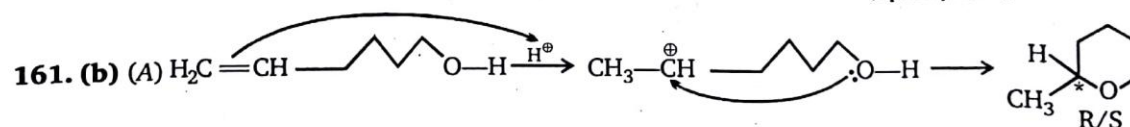
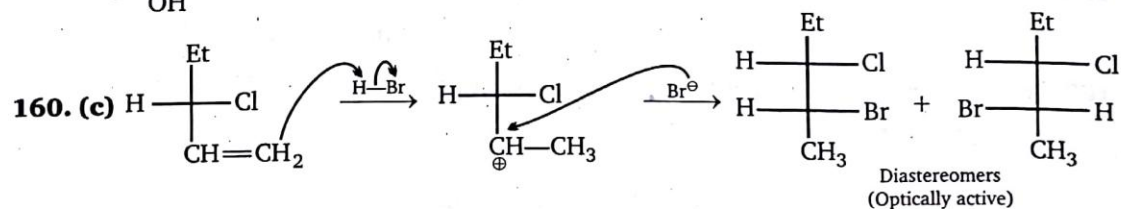
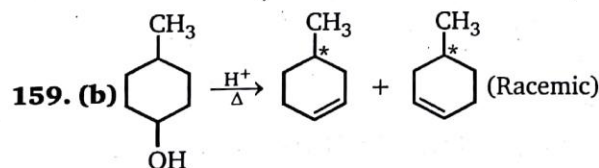
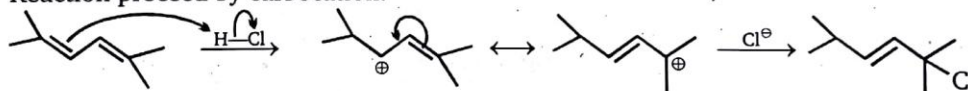
158. (a) Reaction proceed by carbocation.

$\xrightarrow{H-Cl}$ $\longleftrightarrow$ $\xrightarrow{Cl^{\ominus}}$ Cl

159. (b) CH_3, OH $\xrightarrow[\Delta]{H^+}$ CH_3 + CH_3 (Racemic)

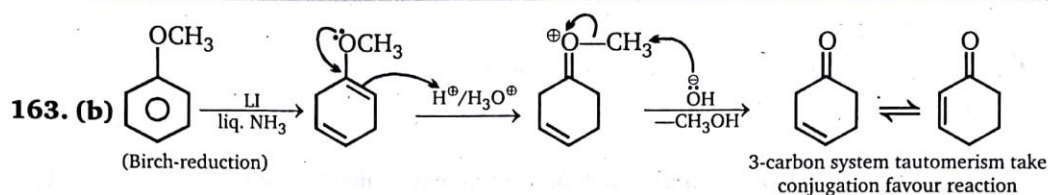
160. (c) $H-C(Et)(Cl)-CH=CH_2 \xrightarrow{H-Br} H-C(Et)(Cl)-\overset{\oplus}{C}H-CH_3 \xrightarrow{Br^{\ominus}}$ (H, Cl / H, Br; Et, CH_3) + (H, Cl / Br, H; Et, CH_3)

Diastereomers
(Optically active)

161. (b) (A) $H_2C=CH-\!\!\!\!\!\sim\!\!\sim\!\!\sim-O-H \xrightarrow{H^{\oplus}} CH_3-\overset{\oplus}{C}H-\!\!\sim\!\!\sim\!\!\sim-\ddot{O}-H \longrightarrow$ H, CH_3, O, R/S

(attack on sp^2-hybridzed carbon) and formation of chiral centre.

∴ Racemic mixture

162. (c) 3 mole of alkene reacts with 1 mole of BH_3

∴ 2 mole of alkene $\longrightarrow$ 2/3 mole of BH_3

163. (b) Anisole $\xrightarrow[\text{liq. } NH_3]{\text{Li}}$ (Birch-reduction) $\xrightarrow{H^{\oplus}/H_3O^{\oplus}}$ $\xrightarrow[-CH_3OH]{\overset{\ominus}{O}H}$ 3-carbon system tautomerism take conjugation favour reaction in forward direction.

164. (d) low conc. of Br_2 and high temperature favour substitution reaction, proceed through free radical.

∴ Substitution will be major product.

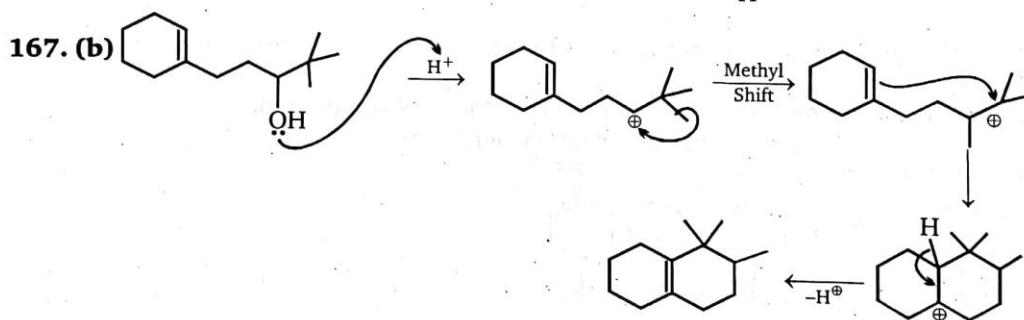
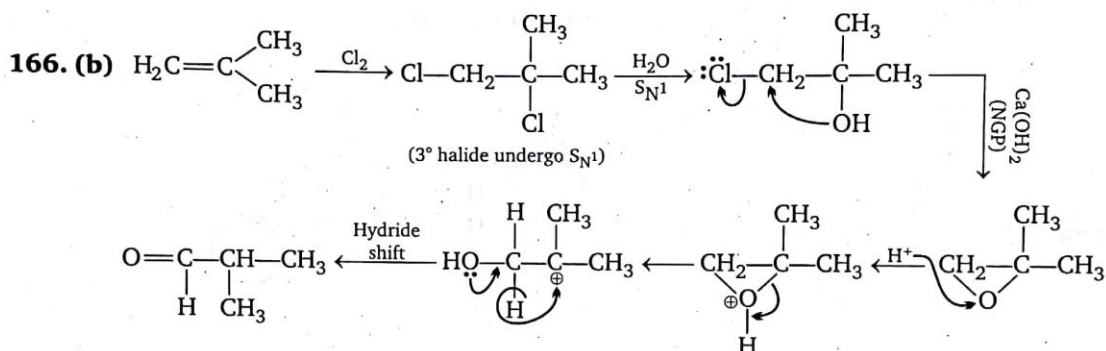
165. (d) In (a) E_2 reaction take place.

In (b) dehydration take place.

In (c) alkyne is more reactive than alkene toward catalytic reductions.

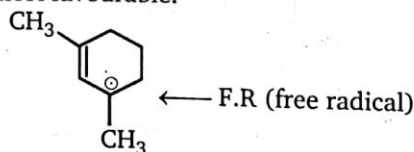
166. (b) $H_2C=C(CH_3)_2 \xrightarrow{Cl_2} Cl-CH_2-C(CH_3)(Cl)-CH_3 \xrightarrow[S_N1]{H_2O} Cl-CH_2-C(CH_3)(OH)-CH_3 \xrightarrow[\text{(NGP)}]{Ca(OH)_2}$ epoxide $\xrightarrow{H^+}$ $CH_2-C(CH_3)-CH_3$ with $\overset{\oplus}{O}H$ $\longrightarrow HO-CH(H)-\overset{\oplus}{C}(CH_3)-CH_3 \xrightarrow{\text{Hydride shift}} O=C(H)-CH(CH_3)-CH_3$

(3° halide undergo S_N1)

167. (b) $\xrightarrow{H^+}$ $\xrightarrow{\text{Methyl Shift}}$ $\longrightarrow$ $\xrightarrow{-H^{\oplus}}$

168. (a) Reaction-proceed through stable free radical.

∴ formation of stable 3° free radical at (a)

∴ Bromination of (a) is most favourable.

CH_3, CH_3 ⟵ F.R (free radical)

169. (c) Iso-butene is most stable isomer of butene.

∴ It have least heat of combustion.

170. (b) CO_3H, Cl (meta-chloro per benzoic acid)

will act as on electrophile and attack on that alkene which has more electron density.

∴ More α-hydrogen

171. (b) OH, OH (Enantiomer) + mirror image

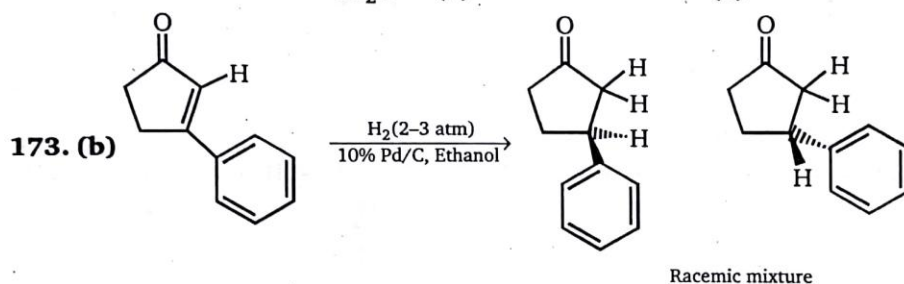
172. (d) Reactant on ozonolysis give

$CH_3—CH(CO_2H)—(CH_2)_3—CHO$ (*A*) $\quad CH_3—CH_2—CH_2—CHO$ (*B*)

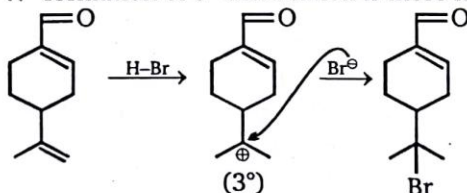
173. (b) O, H $\xrightarrow[\text{10\% Pd/C, Ethanol}]{H_2(2\text{–}3\text{ atm})}$ O, H, H, H + O, H, H, H

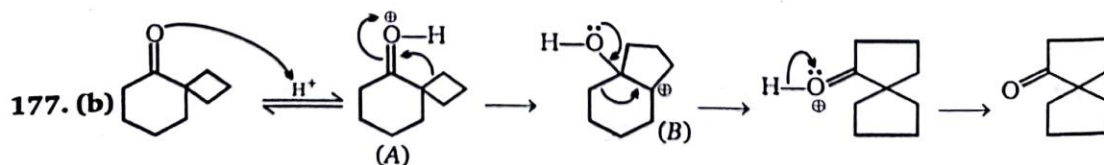
Racemic mixture

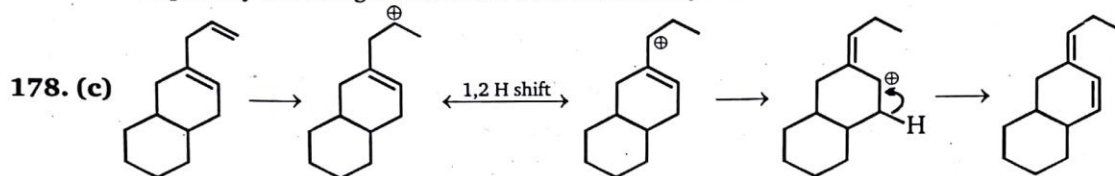
Notice that the benzene ring is inert to these conditions; hydrogenation of benzene is discussed.

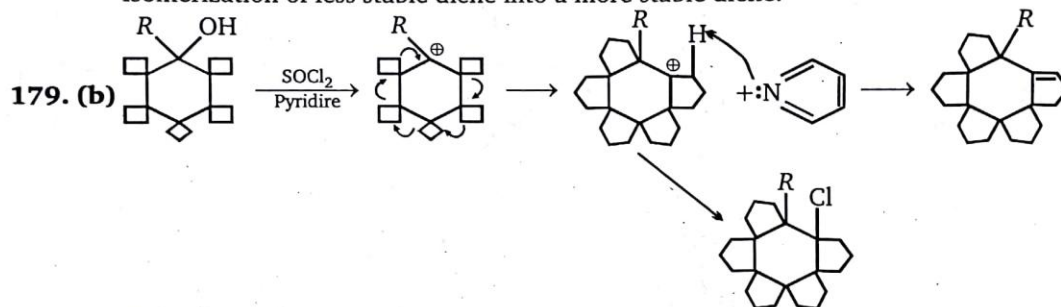
174. (c) Rate determining step of the reaction is formation of carbocation.

∴ formation of 3° carbocation is more favourable.

O $\xrightarrow{\text{H–Br}}$ O, ⊕ (3°) $\xrightarrow{Br^{\ominus}}$ O, Br

175. (b) less stable alkene (less α-hydrogen) will undergo reduction first.

176. (b) OH $\xrightarrow{\text{MCPBA}}$ O, H, OH + mirror image (Chiral center)

177. (b) O $\underset{}{\overset{H^+}{\rightleftharpoons}}$ ⊕O—H (*A*) ⟶ H—Ö, ⊕ (*B*) ⟶ H—Ö⊕ ⟶ O

The decrease of ring strain can provide a driving force strong enough to overcompensete for the conversion of a more stable into less stable cationic centre, the carbooxonium ion (*A*) rearranges into the carbonium ion (*B*) because of the release of cyclo butene strain (26 kcal/mol) in the formation of the cyclopentane (ring strain of about 5 cal/mol) cation *B* stablizer itself by way of another 1,2 rearrangement. The resulting action (c) has comparebly little ring strain but is an electronically favourable carboxonium ion.

178. (c) → 1,2 H shift → → H →

Isomerization of less stable diene into a more stable diene.

179. (b) R, OH $\xrightarrow[\text{Pyridire}]{SOCl_2}$ R ⊕ → R, H, ⊕ + :N → R; R, Cl

180. (c) Three times ring expansion.

181. (b) COOH $\xrightarrow[\text{liq. } NH_3]{Na}$ CO_2H (major), $\xrightarrow[\text{liq. } NH_3]{Na}$ (major) (Two individual benzene is very stable)

$\xrightarrow[NH_3]{Na}$

182. (b) OR $\xrightarrow{BH_3}$ δ⊕ H δ⊖ B—H H OR → H BH$_2$ OR $\xrightarrow[\text{then } H_2SO_4,\ HO^{\ominus}]{\text{2 mole of reactant}}$ OH OR

183.(c) (*A*) = ÖH, Cl: $\xrightarrow{NaOH}$ O

(N.G.P.)
(Neighbouring Group Participation)

184. (c) $H^{\oplus}$ → ⟷ 1,2 methyl shift → (major)

185. (c) $H^{\oplus}$ → ⟷ 1,2-methyl shift → → 1,2-methyl shift → → CH_3 CH_3 CH_3 (minor) (due to steric repulsion)

186. (b) + $\overset{82}{Br}$—$\overset{82}{Br}$ $\xrightarrow{CCl_4}$ Br^{82} Br Br^{82}

(Anti-addition take place)

187. (a) $\xrightarrow[CCl_4]{Br_2}$ + Diastereoisomer

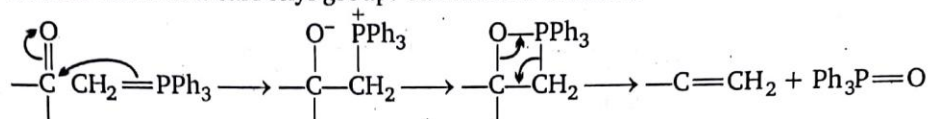
Chiral center does not involve in the reaction

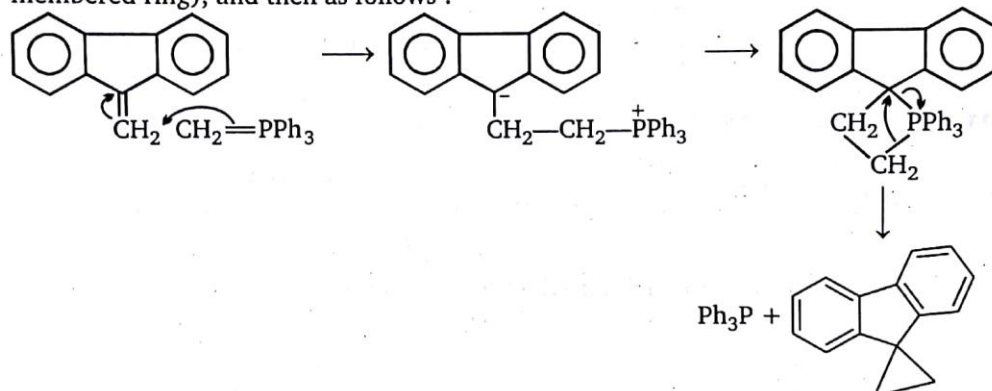
188. (b) Un-symmetrical alkene undergo halogenation to give racemic mixture.

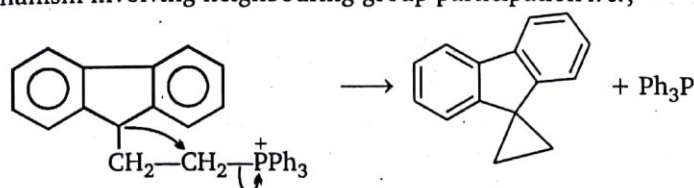
189. (b) $\xrightarrow{Ph_3P=CH_2}$ Ph_3PO +

$\xrightarrow{Ph_3P=CH_2}$ Ph_3P +

Since there is no carbonyl group in the first product, the double bond of the exocyclic methylene group has reacted with methylenephosphorane. We may therefore propose a mechanism based on the assumption that the exocyclic double bond behaves like the double bond in a carbonyl group. The latter reaction is

$$-\overset{O}{\overset{\|}{C}}-\ CH_2=PPh_3 \longrightarrow -\overset{O^-}{\underset{|}{C}}-\overset{\overset{+}{P}Ph_3}{CH_2} \longrightarrow -\overset{O-PPh_3}{\underset{|}{C}-CH_2} \longrightarrow -C=CH_2 + Ph_3P=O$$

However, in the case under consideration, there is no oxygen atom, phosphine and not phosphine oxide is eliminated, and a single and not a double bond is formed with the methylene group. This can be accommodated by replacing O^- by $>C^-$ (of the five - membered ring), and then as follows :

$CH_2\ CH_2=PPh_3$ ⟶ $CH_2-CH_2-\overset{+}{P}Ph_3$ ⟶ $CH_2\ \overset{+}{P}Ph_3$ / CH_2 ⟶ Ph_3P +

In this sequence, we have proposed a complete parallel with the carbonyl group and this results in the formation of a spiro-compound containing phosphorus in one ring. The final product is also a spiro-compound, but since this contains a three-membered ring, it could be argued that this is less stable than its precursor – which contains a four - membered ring. This can be overcome by assuming that the three - membered ring is formed directly, the mechanism involving neighbouring group participation *i. e.*,

$CH_2-CH_2-\overset{+}{P}Ph_3$ ⟶ + Ph_3P

This route would be energetically more favourable than the other one and so is the more likely one.

190. (b) $CH_3—CH_2—CH_2—CH_2—C(CH_3)_2—CH_2—\ddot{O}—H \xrightarrow{H^\oplus} CH_3—CH_2—CH_2—CH_2—C(CH_3)_2—\overset{\oplus}{C}H_2$

n-butyl shift: $(\overset{\alpha}{C}H_3)_2\overset{\oplus}{C}—CH_2(CH_2)_2—CH_2—CH_3$ (8α)

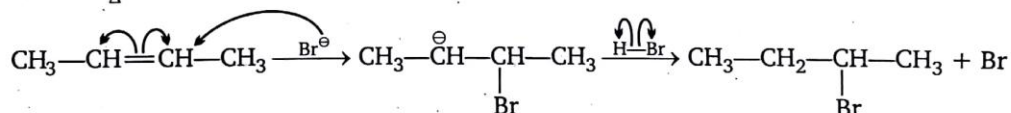
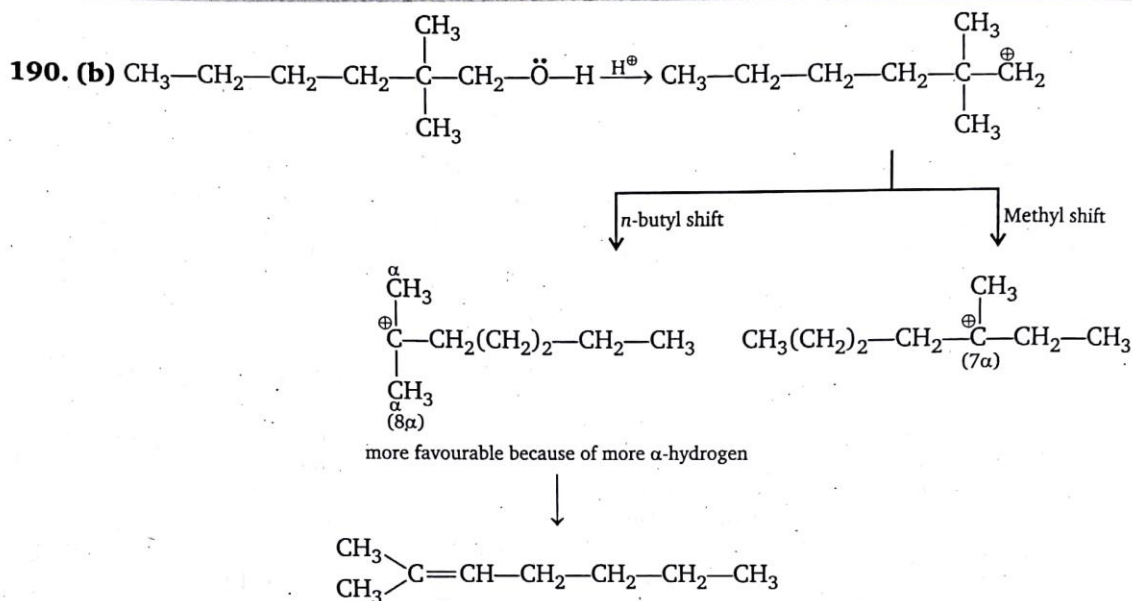
more favourable because of more α-hydrogen

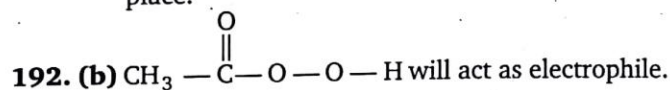
Methyl shift: $CH_3(CH_2)_2—CH_2—\overset{\oplus}{C}(CH_3)—CH_2—CH_3$ (7α)

$\downarrow$

$(CH_3)_2C{=}CH—CH_2—CH_2—CH_2—CH_3$

191. (a) $R_2O_2 \xrightarrow[\Delta]{} 2RO^\ominus + H—Br \longrightarrow ROH + Br^\ominus$

$CH_3—CH{=}CH—CH_3 \xrightarrow{Br^\ominus} CH_3—\overset{\ominus}{C}H—CH(Br)—CH_3 \xrightarrow{H—Br} CH_3—CH_2—CH(Br)—CH_3 + Br$

Due to attack on sp^2-hybridized reactant and formation of chiral centre, racemization take place.

192. (b) $CH_3—\overset{O}{\overset{\|}{C}}—O—O—H$ will act as electrophile.

∴ alkene having more α-hydrogen is better nucleophile it will undergo reaction.

193. (c) Alkene (*A*) must be symmetrical alkene. Which give racemic mixture an anti-addition and meso-compound is syn-addition.

∴ *cis*-4-octene is the answer.

194. (b) Witting reaction

[epoxide (H, Me / Me, H)] + PPh_3 ⟶ [$\overset{\ominus}{O}$, Me, H / H, Me, $\overset{\oplus}{P}Ph_3$] ⟶ [$\overset{\ominus}{O}$ $\overset{\oplus}{P}Ph_3$ / H, Me, H, Me] ⟶ [oxaphosphetane $\overset{\ominus}{O}$—$\overset{\oplus}{P}Ph_3$ / H, Me, H, Me]

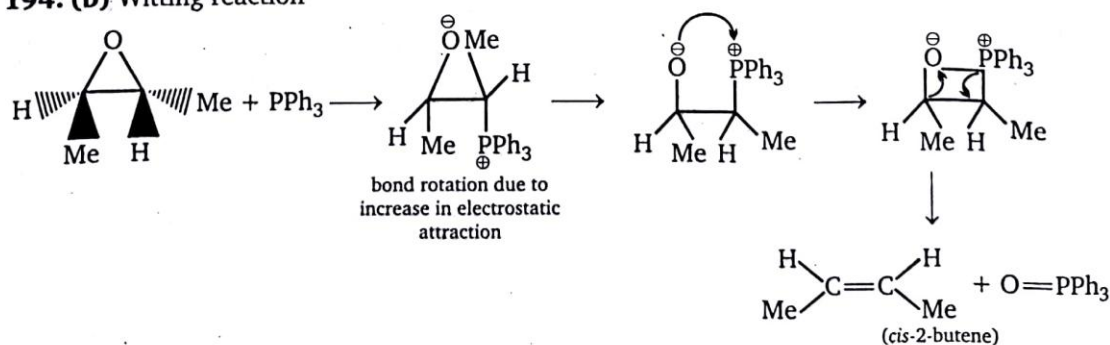
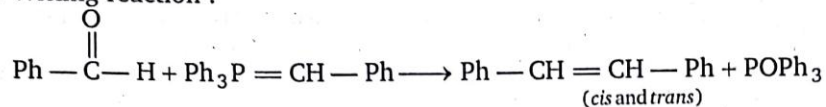
bond rotation due to increase in electrostatic attraction

$\downarrow$

$(H)(Me)C{=}C(H)(Me) + O{=}PPh_3$

(*cis*-2-butene)

195. (c) Witting reaction :

$$Ph-\overset{\overset{O}{\parallel}}{C}-H + Ph_3P=CH-Ph \longrightarrow \underset{(cis\ and\ trans)}{Ph-CH=CH-Ph} + POPh_3$$

196. (c) $a = Ag_2O, H_2O_2$ (Oxidative ozonolysis)

$b = Zn/CH_3CO_2H$ and CH_3-S-CH_3 (reductive ozonolysis)

$c = LiAlH_4$ and $NaBH_4$ (Corresponding alcohol will formed)

197. (b) Addition of CH_3OH, acc. to Markovnikoff's rule take place

∴ 1-methyl-1-methoxycyclohexane (OCH_3 and CH_3 on the same ring carbon)

198. (a)

$$CH_3-\overset{\overset{\ominus\oplus}{ONa}}{C}=CH_2 + H-C\equiv C-H \longrightarrow CH_3-\overset{OH}{C}=CH_2 + H-C\equiv \overset{\ominus\oplus}{C}Na$$

(Acid-base reaction)

tautomerism

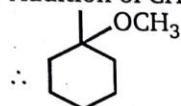
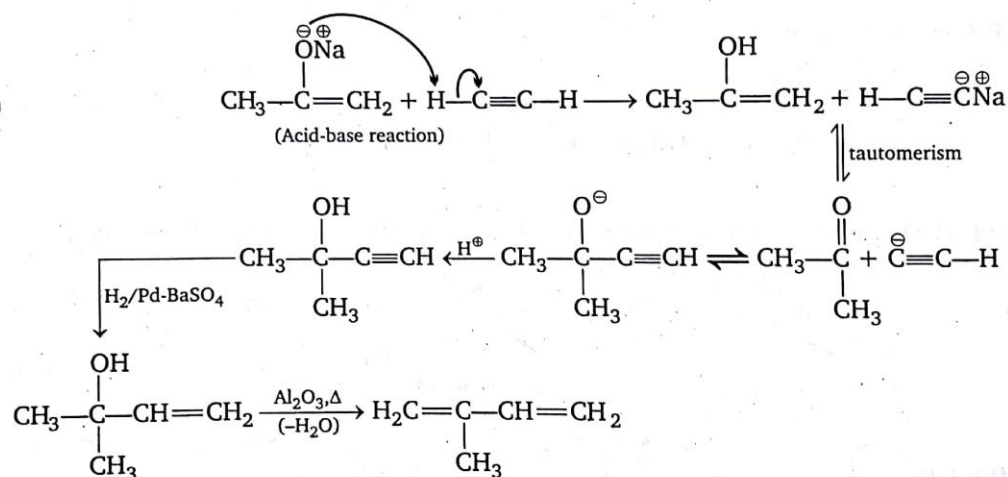
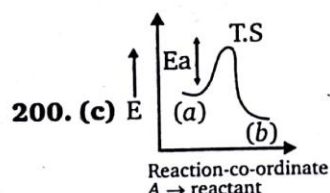
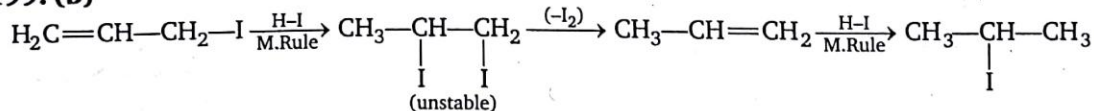
$$CH_3-\underset{CH_3}{\overset{OH}{C}}-C\equiv CH \xleftarrow{H^{\oplus}} CH_3-\underset{CH_3}{\overset{O^{\ominus}}{C}}-C\equiv CH \rightleftharpoons CH_3-\underset{CH_3}{\overset{\overset{O}{\parallel}}{C}} + \overset{\ominus}{C}\equiv C-H$$

$H_2/Pd\text{-}BaSO_4$

$$CH_3-\underset{CH_3}{\overset{OH}{C}}-CH=CH_2 \xrightarrow[(-H_2O)]{Al_2O_3,\Delta} H_2C=\underset{CH_3}{C}-CH=CH_2$$

199. (b)

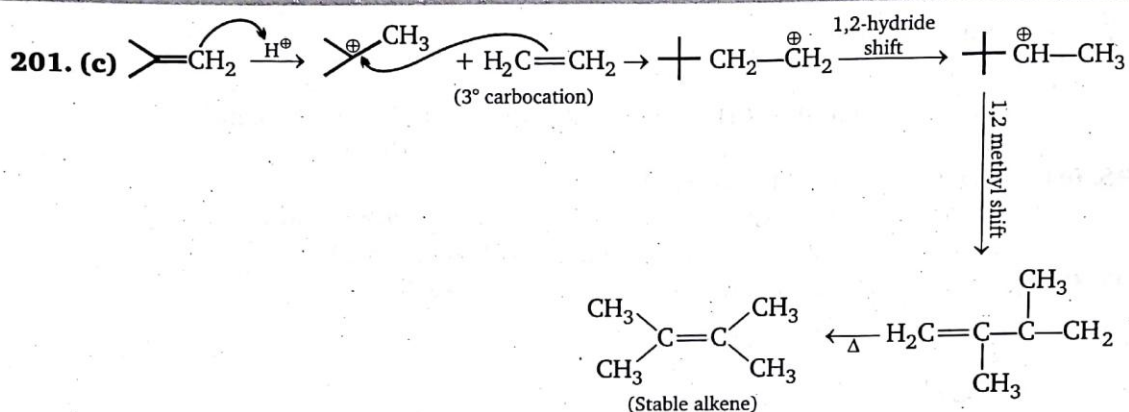
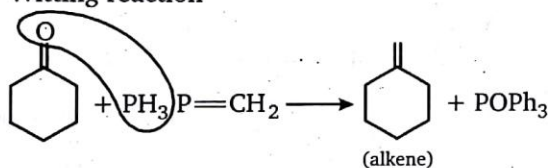
$$H_2C=CH-CH_2-I \xrightarrow[M.Rule]{H-I} \underset{(unstable)}{CH_3-\underset{I}{CH}-\underset{I}{CH_2}} \xrightarrow{(-I_2)} CH_3-CH=CH_2 \xrightarrow[M.Rule]{H-I} CH_3-\underset{I}{CH}-CH_3$$

200. (c)

more the stable reactant and more will activation energy less will be rate constant more the stable transition stable less will activation energy more is rate of reaction.

201. (c) $\xrightarrow{H^\oplus}$ (3° carbocation) + $H_2C{=}CH_2$ → CH_2—$\overset{\oplus}{C}H_2$ $\xrightarrow[\text{shift}]{\text{1,2-hydride}}$ $\overset{\oplus}{C}H$—CH_3 $\xrightarrow{\text{1,2 methyl shift}}$ $H_2C{=}C$—$C(CH_3)$—CH_2 $\xrightarrow{\Delta}$ $(CH_3)_2C{=}C(CH_3)_2$

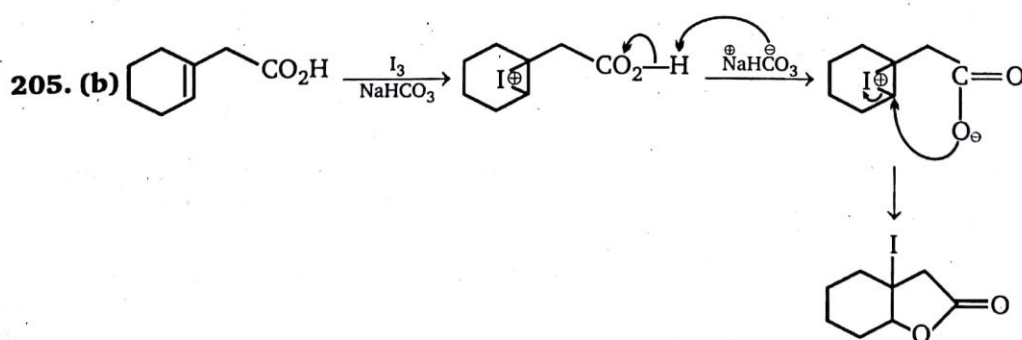
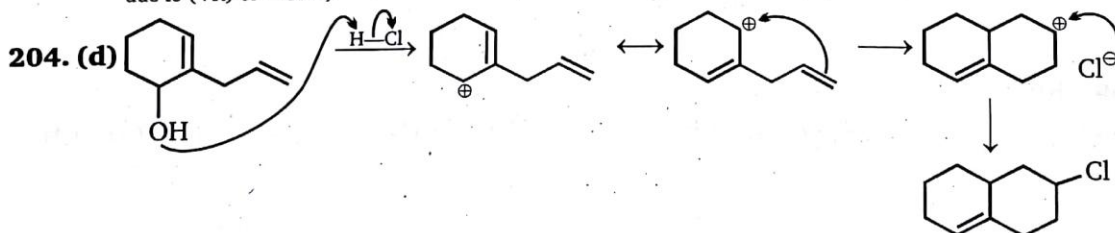
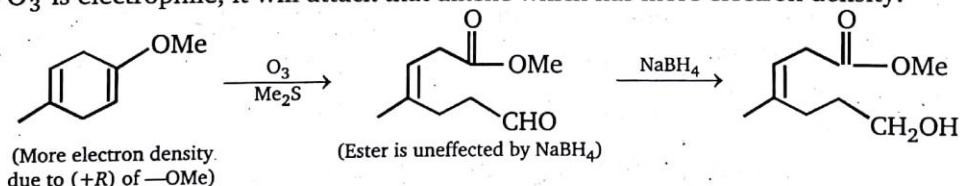
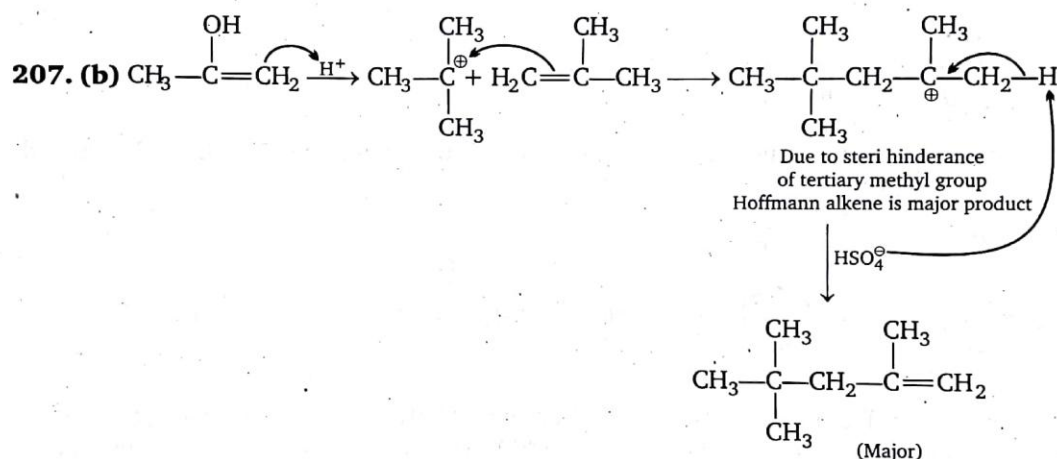
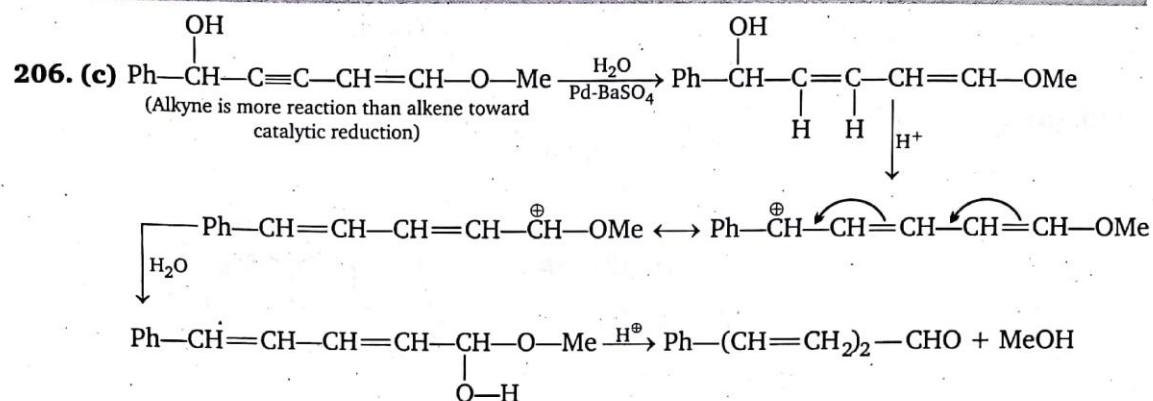
(Stable alkene)

202. (c) Witting reaction

+ $PH_3P{=}CH_2$ ⟶ (alkene) + $POPh_3$

203. (b) O_3 is electrophile, it will attack that alkene which has more electron density.

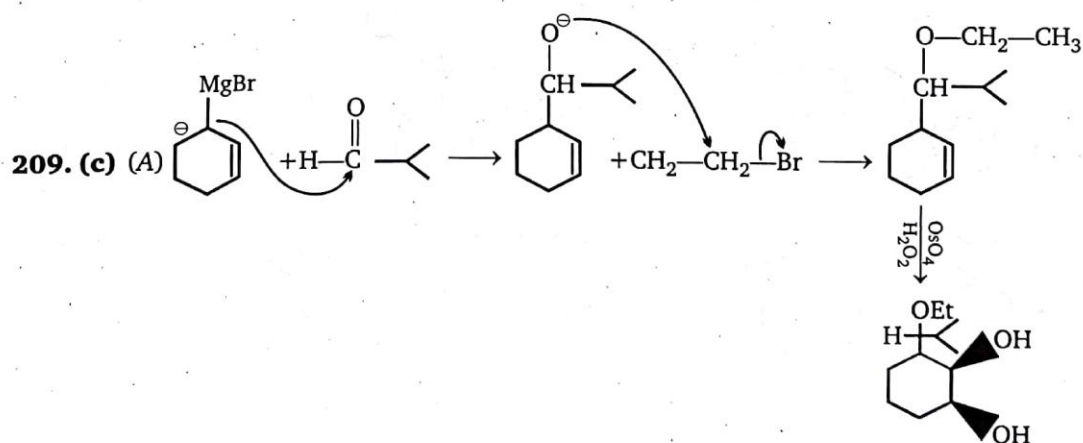
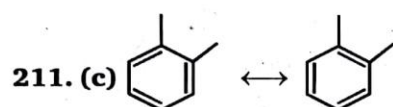
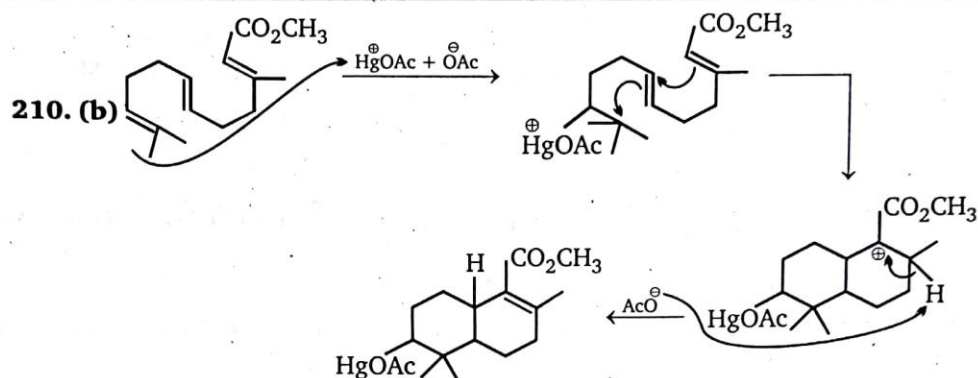
(More electron density due to (+*R*) of —OMe) $\xrightarrow[Me_2S]{O_3}$ OMe, CHO (Ester is uneffected by $NaBH_4$) $\xrightarrow{NaBH_4}$ OMe, CH_2OH

204. (d) OH $\xrightarrow{H—Cl}$ ⊕ ⟷ ⊕ ⟶ ⊕ $Cl^\ominus$ ⟶ Cl

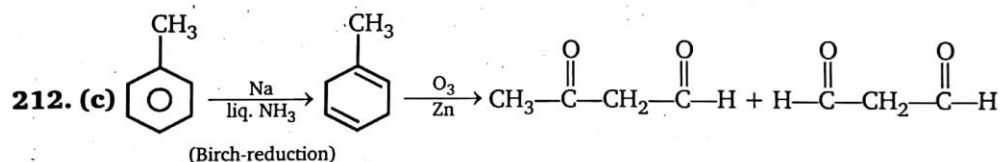
205. (b) CO_2H $\xrightarrow[NaHCO_3]{I_3}$ I⊕ CO_2—H $\xrightarrow{\overset{\oplus}{N}aH\overset{\ominus}{C}O_3}$ I⊕ C=O, $O^\ominus$ ⟶ I, =O, O

208. (b) Option (b) on ozonolysis give desired product.

209. (c) (*A*) cyclohexenyl MgBr (⊖) + H—C(=O)—CH(CH$_3$)$_2$ ⟶ cyclohexenyl—CH(O$^{\ominus}$)—CH(CH$_3$)$_2$ + CH$_2$—CH$_2$—Br ⟶ cyclohexenyl—CH(O—CH$_2$—CH$_3$)—CH(CH$_3$)$_2$ $\xrightarrow{OsO_4,\ H_2O_2}$ H—C(OEt)(CH(CH$_3$)$_2$)—cyclohexane with two OH (cis-diol)

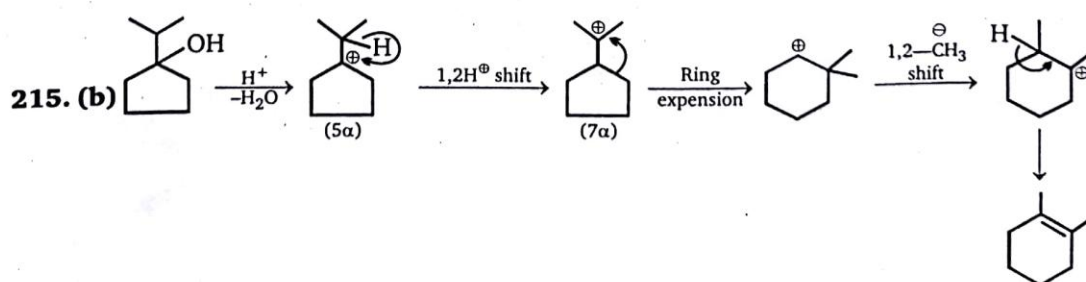
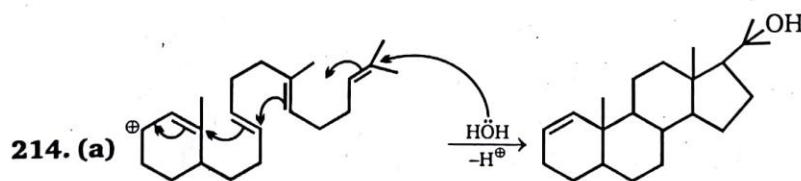
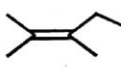
210. (b) CO_2CH_3 $\xrightarrow{\overset{\oplus}{Hg}OAc + \overset{\ominus}{O}Ac}$ CO_2CH_3, $\overset{\oplus}{Hg}OAc$ → CO_2CH_3, H, HgOAc $\xrightarrow{Ac\overset{\ominus}{O}}$ H, CO_2CH_3, HgOAc

211. (c) ⟷

are the canonical structure of *o*-xylene, which on ozonolysis gave 3 mole of glyoxal and 2 mole of pyrualdehyde.

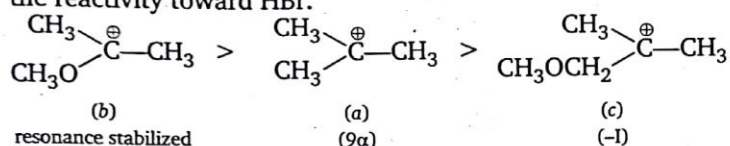
212. (c) CH_3 $\xrightarrow[\text{liq. } NH_3]{Na}$ CH_3 $\xrightarrow[Zn]{O_3}$ $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-H + H-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-H$

(Birch-reduction)

213. (b) Once a small amount of OsO_4 is used up the Os (VI) by product is oxidized with is the reaction mixture by the amine oxide to re-form OsO_4, thus, a catalytic amount of OsO_4 can be used and the amine oxide acts as the ultimate oxidant.

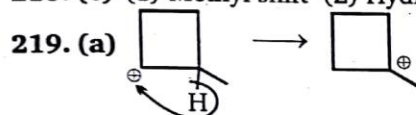
214. (a) $\xrightarrow[-H^{\oplus}]{H\ddot{O}H}$ OH

215. (b) OH $\xrightarrow[-H_2O]{H^+}$ (5α) $\xrightarrow{1,2H^{\oplus}\text{ shift}}$ (7α) $\xrightarrow{\text{Ring expension}}$ $\xrightarrow{1,2-\overset{\ominus}{C}H_3 \text{ shift}}$ H →

216. (b) Formation of carbocation is the rate determining step more the stable carbocation more is the reactivity toward HBr.

$$(CH_3)(CH_3O)\overset{\oplus}{C}{-}CH_3 > (CH_3)_2\overset{\oplus}{C}{-}CH_3 > (CH_3)(CH_3OCH_2)\overset{\oplus}{C}{-}CH_3$$

(b) resonance stabilized; (a) (9α); (c) (–I)

217. (d) gives more stable is carbocation and this alkene is less stable than

218. (c) (1) Methyl shift (2) Hydride shift (3) Hydride shift (4) Hydride shift.

219. (a) → (H)

(b) methyl shift (c) No rearrangement (d) Ring expension.

220. (b) Product *a* is

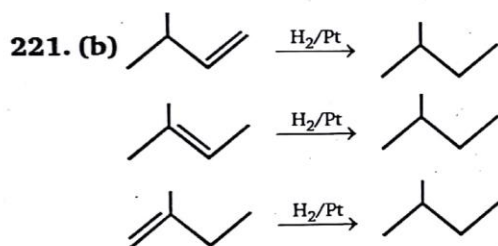
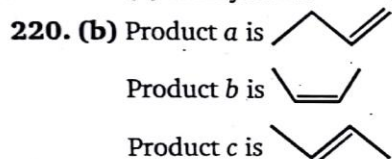
Product *b* is

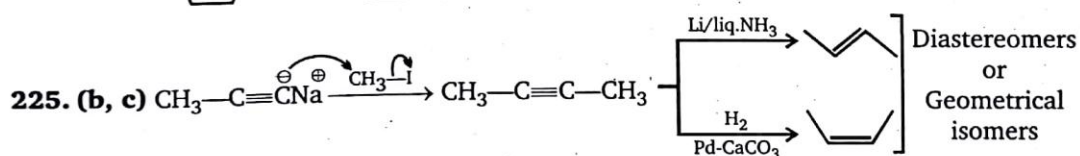
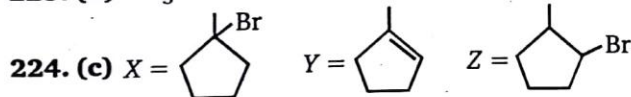
Product *c* is

221. (b) $\xrightarrow{H_2/Pt}$

$\xrightarrow{H_2/Pt}$

$\xrightarrow{H_2/Pt}$

222. (c)

is stable carbocation due to presence of σ-resonance so it will not rearrange.

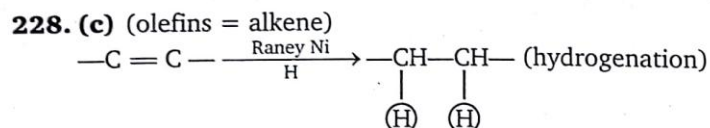
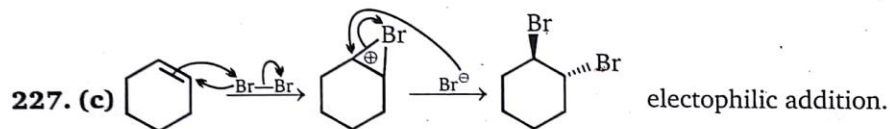
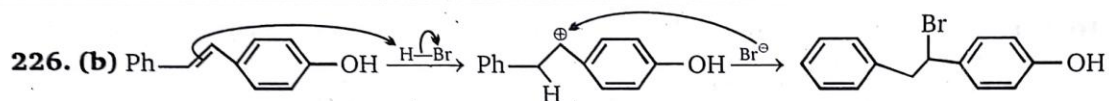
223. (d) SbF_5 is an electrophile which accept the pair of electron in vacant *d*-orbital.

224. (c) $X =$ Br $Y =$ $Z =$ Br

225. (b, c) $CH_3{-}C{\equiv}\overset{\ominus}{C}\overset{\oplus}{Na} \xrightarrow{CH_3{-}I} CH_3{-}C{\equiv}C{-}CH_3$ $\xrightarrow{Li/liq.NH_3}$ / $\xrightarrow[Pd\text{-}CaCO_3]{H_2}$ Diastereomers or Geometrical isomers

226. (b) Ph—CH=CH—C_6H_4—OH $\xrightarrow{H—Br}$ Ph—CH_2—$\overset{\oplus}{C}H$—C_6H_4—OH $\xrightarrow{Br^{\ominus}}$ C_6H_5—CH_2—CH(Br)—C_6H_4—OH

227. (c) cyclohexene $\xrightarrow{Br—Br}$ bromonium ion $\xrightarrow{Br^{\ominus}}$ trans-1,2-dibromocyclohexane electophilic addition.

228. (c) (olefins = alkene)

$$—C=C— \xrightarrow[H]{\text{Raney Ni}} —\underset{(H)}{CH}—\underset{(H)}{CH}— \text{ (hydrogenation)}$$

Level-2

Comprehensive-1

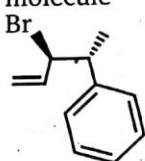
1. (i) Markovnikoff 's addition and it is minor product.
(ii) Halogenation of alkene
(iii) Halohydrin formation by (HOBr)
(iv) $C_1H \longrightarrow$ oxymercuration-Demercuration reaction.
(v) Dihydroxylation

2. (a) Halogenation
(b) Oxymercuration-De-mercuration reaction (OMDM reaction)
(c) Hydroboration-oxidation reaction (HBO reaction)

(e) $CH_3CH=CH_2 \xrightarrow{\text{OMDM}} CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[\text{oxidising agent}]{\text{HOBr}} CH_3-CH_2-CHO$

(f) Halohydrin formation
(g) Markovnikoff addition
(h) Oxidation reaction
(i) $CH_3-CH=CH_2 \xrightarrow{\text{HBO}} CH_3-CH_2-CH_2-OH \xrightarrow[\text{Darzene process}]{SOCl_2} CH_3-CH_2-CH_2-Cl + SO_2 + HCl$
(j) Halogenation and elimination.

3. Reaction 1: B, D; Reaction 2: E, F, C Reaction 3: I, A
Reaction 4: L, G; Reaction 5: B, L, C

4. Match the reagents a-j with products A-J. There is one best product for each reaction. This molecule

is the starting material for all reactions in problem. Do the ones you know first and then tackle the rest by deductive reasoning

Products	Reagents	Option
(A)	(a) H_2O heat, pH 7.	C, S_N1 reaction
(B) HO, Br, HO	(b) $F_3C-C(=O)-O-OH$	D, Oxidation of alkene

(C) OH OH

(c) tBuOK, polar aprotic solvent

A E_2 reaction elimination bimolecular

(D) Br O

(d) (1) O_3, ether
(2) $H_2O, NaOH, H_2O_2$

F Oxidative ozonolysis

(E) O

(e) Br_2, CCl_4

I Halogenation of alkene

(F) Br O HO

(f) NBS, $h\nu$, CCl_4

J Benzylic substitution

(G) Br

(g) (1) $H_3O(+)$
(2) NaOH, H_2O

E hydration followed by N.G.P.

(H) Br OH

(h) (1) BH_3, ether
(2) H_2O_2

H Hydroboration oxidation

(I) Br Br Br

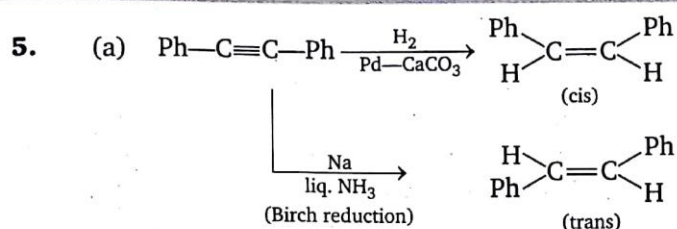
(i) (1) OsO_4
(2) NaOH, H_2O

B Oxidation reaction

(J) Br Br Br Br

(j) (1) PdC, EtOH, H_2

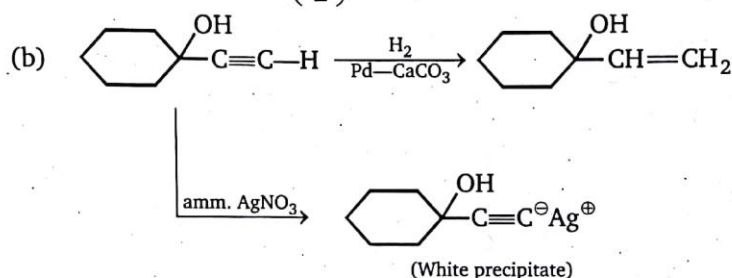
G Reduction reaction

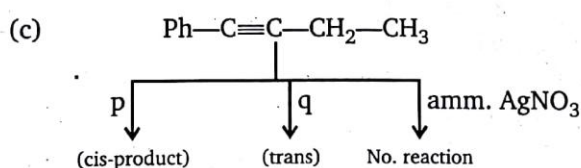
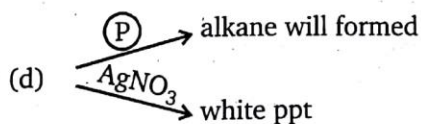
5. (a)

Formula of D.B.E. (Double bond equivalent)

$$DBE = (C+1) - \left(\frac{H + X - N}{2}\right)$$

X = halogen

$$D.B.E. = (14+1) - \left(\frac{10}{2}\right) = 10$$

(b)

D. B. E. = 3

Birch reduction cannot be used for terminal alkyne

(c)

DBE = 6

(d)

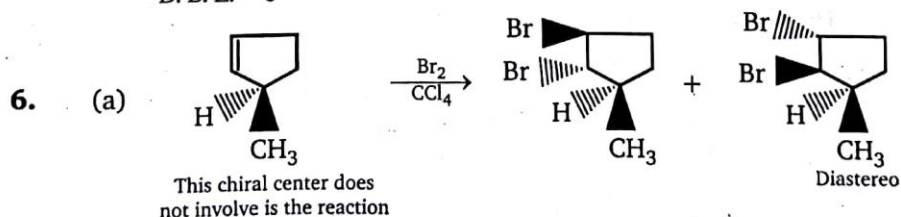
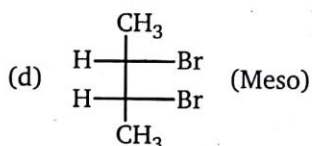
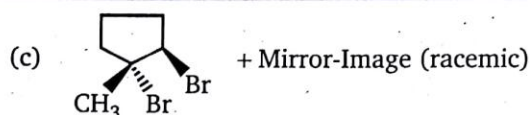
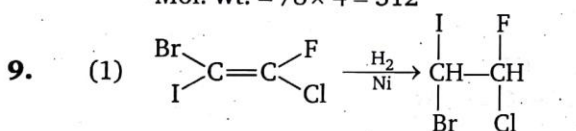
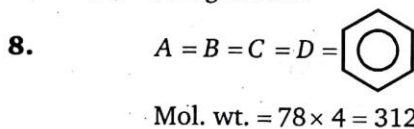
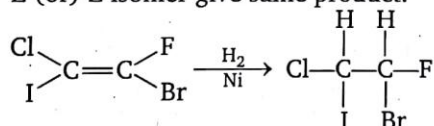
D. B. E. = 6

6. (a)

This chiral center does not involve is the reaction

(b) Un-symmetrical alkene undergo halogenation to give racemic mixture.

(c) CH$_3$ Br Br + Mirror-Image (racemic)

(d) CH$_3$; H—Br; H—Br; CH$_3$ (Meso)

7. (a) OsO_4 will form diol
(b) (HBO)
(c) halohydrin
(d) halogenation

8. $A = B = C = D =$ (benzene)

Mol. wt. $= 78 \times 4 = 312$

9. (1) Br(I)C=C(F)(Cl) $\xrightarrow[Ni]{H_2}$ CH(I)(Br)—CH(F)(Cl)

E (or) Z isomer give same product.

Cl(I)C=C(F)(Br) $\xrightarrow[Ni]{H_2}$ Cl—CH(I)—CH(Br)—F

E (or) Z isomer give same product.

Cl(Br)C=C(F)(I) $\xrightarrow[Ni]{H_2}$ CH(Cl)(Br)—C(F)(I)—H

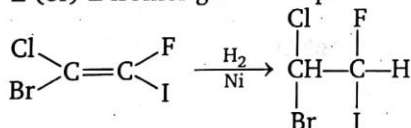
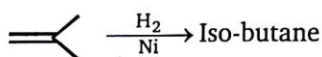
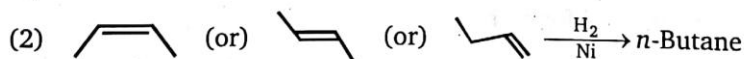
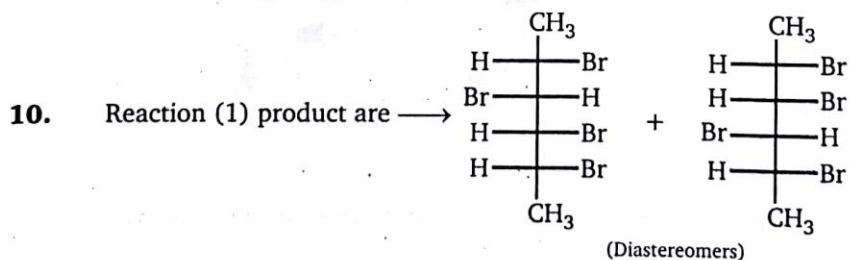
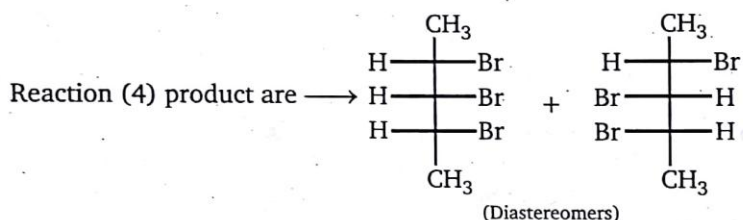
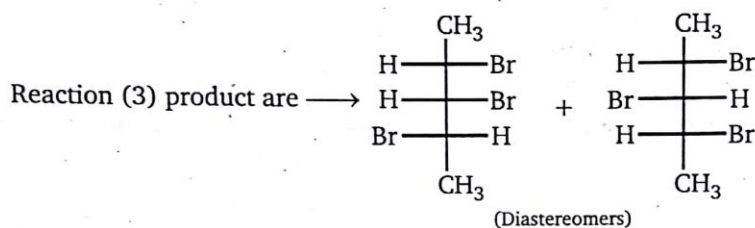
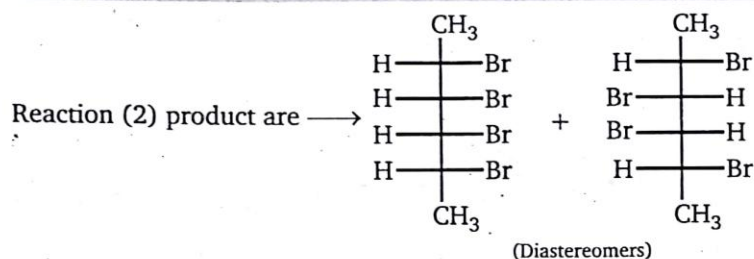
E (or) Z isomer give same product. $(A = 3)$

(2) (cis-2-butene) (or) (trans-2-butene) (or) (1-butene) $\xrightarrow[Ni]{H_2}$ n-Butane

(isobutene) $\xrightarrow[Ni]{H_2}$ Iso-butane

$(B = 2)$ $\therefore$ $A + B = 5$

10. Reaction (1) product are $\longrightarrow$ CH$_3$; H—Br; Br—H; H—Br; H—Br; CH$_3$ + CH$_3$; H—Br; H—Br; Br—H; H—Br; CH$_3$

(Diastereomers)

Reaction (2) product are
(Diastereomers)
Reaction (3) product are
(Diastereomers)
Reaction (4) product are
(Diastereomers)
Sum of products (P + Q + R + S) = 8
11. A-b, B-c, C-d, D-b, E-d, F-d
(A)
Markov hikov addition
(octet complete carbocation)
(B)
exothermic (1 π-bond breaks and 2σ-bonds are formed)
(C) (a)
HCl 0°C
Shift
(b)
shift

(c) $Ph—CH_2—CH=CH_2 \xrightarrow[CCl_4]{HBr} Ph—CH(H)—\overset{\oplus}{C}H—CH_3 \xrightarrow[Shift]{H^{\ominus}} Ph—\overset{\oplus}{C}H—CH_2CH_3$

(D) 1-methylcyclohexene:

- $\xrightarrow[H_2O]{HBr}$ 1-methylcyclohexyl cation $\xrightarrow{H_2O}$ 1-methylcyclohexanol (CH_3, OH) + HBr
- $\xrightarrow[CH_3OH]{HBr}$ 1-methylcyclohexyl cation $\xrightarrow{CH_3OH}$ (CH_3, OCH_3) + HBr
- $\xrightarrow[D_2O]{HBr}$ 1-methylcyclohexyl cation $\xrightarrow{D_2O}$ (CH_3, OD) + DBr

(E) (a) 2-bromobutane* (±) (b) 2-bromobutane* (±) (c) 2-bromobutane* (±)

(F) (a) 2-methyl-1-methylenecyclohexane $\xrightarrow[CCl_4]{HBr}$ 1-bromo-1,2-dimethylcyclohexane (CH_3, Br, CH_3) + 1-bromo-1,2-dimethylcyclohexane (CH_3, Br, CH_3) (diastereomers)

(b) $C_6H_5—CH=CH—C(H)(D)CH_3 \xrightarrow[CCl_4]{HBr} C_6H_5—C(H)(Br)—CH_2—C(H)(D)CH_3 + C_6H_5—C(Br)(H)—CH_2—C(H)(D)CH_3$

(c) 3-bromocyclohexene $\xrightarrow[CCl_4]{HBr}$ 1,3-dibromocyclohexane (Br, Br) + 1,3-dibromocyclohexane (Br, Br)

12. A-b, B-b, C-c, D-b, E-b

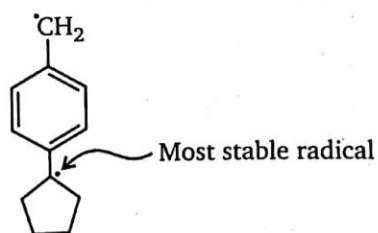
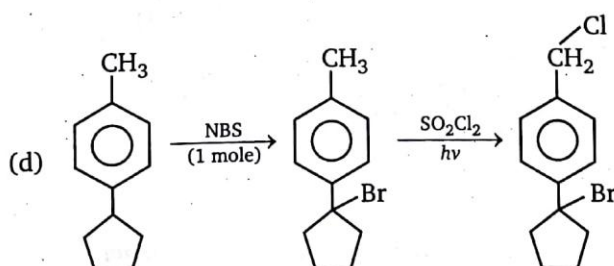
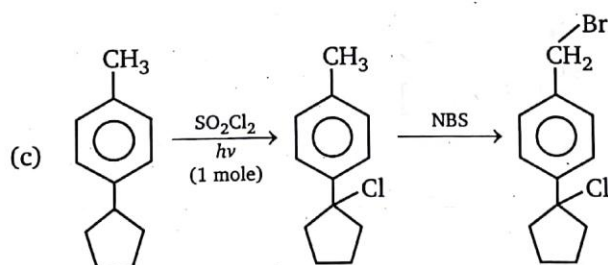
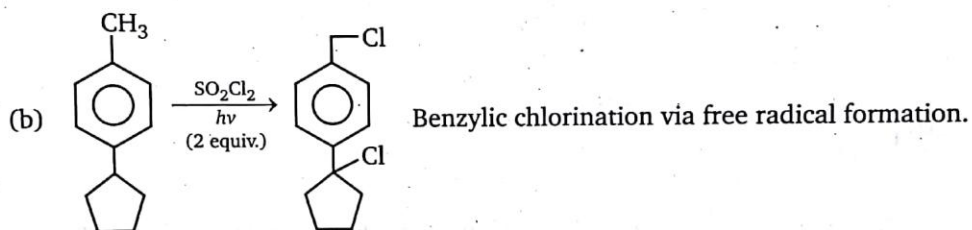
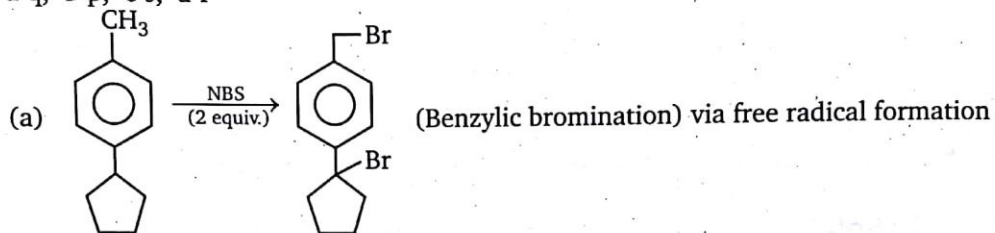
13. a-q, b-p, c-s; d-r

(a) $\xrightarrow[\text{(2 equiv.)}]{\text{NBS}}$ (Benzylic bromination) via free radical formation

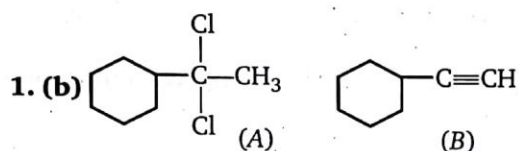
(b) $\xrightarrow[\text{(2 equiv.)}]{SO_2Cl_2,\ h\nu}$ Benzylic chlorination via free radical formation.

(c) CH_3 $\xrightarrow[\text{(1 mole)}]{SO_2Cl_2,\ h\nu}$ Cl $\xrightarrow{\text{NBS}}$ CH_2–Br, Cl

(d) CH_3 $\xrightarrow[\text{(1 mole)}]{\text{NBS}}$ Br $\xrightarrow{SO_2Cl_2,\ h\nu}$ CH_2–Cl, Br

$\dot{C}H_2$ — Most stable radical

4(C) Hydrocarbons (Alkynes)

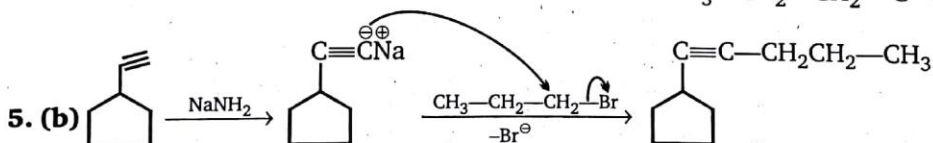
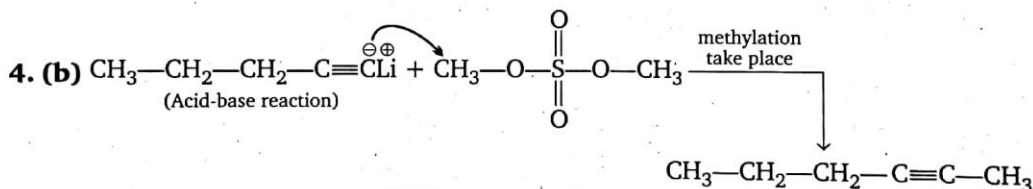
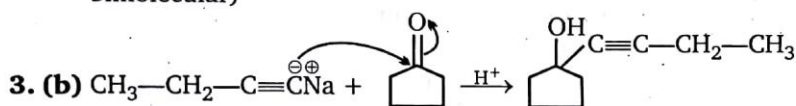
Level-1

1. (b)

2. (b) Formation of vicinal di-halide followed by two consecutive E_2 reaction. (elimination bimolecular)

3. (b) $CH_3—CH_2—C≡\overset{\ominus\oplus}{C}Na$ + cyclopentanone $\xrightarrow{H^+}$ 1-(but-1-ynyl)cyclopentanol (OH, $C≡C—CH_2—CH_3$)

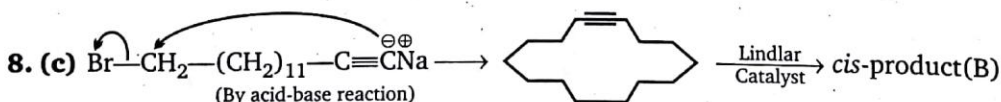
4. (b) $CH_3—CH_2—CH_2—C≡\overset{\ominus\oplus}{C}Li + CH_3—O—SO_2—O—CH_3 \xrightarrow{\text{methylation take place}} CH_3—CH_2—CH_2—C≡C—CH_3$

(Acid-base reaction)

5. (b) ethynylcyclopentane $\xrightarrow{NaNH_2}$ cyclopentyl–$C≡\overset{\ominus\oplus}{C}Na$ $\xrightarrow[-Br^{\ominus}]{CH_3—CH_2—CH_2—Br}$ cyclopentyl–$C≡C—CH_2CH_2—CH_3$

6. (d) All alkyne on catalytic hydrogenation give 3-ethylhexane.

7. (c) Reagent (I) give *trans* product. Reagent (II) and (III) give *cis*-product.

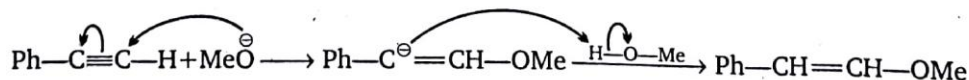
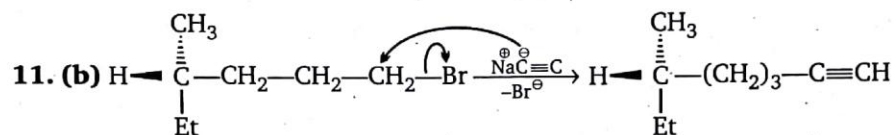
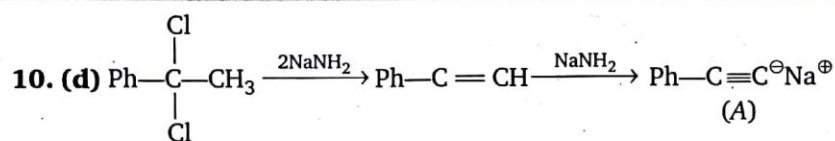
8. (c) $Br—CH_2—(CH_2)_{11}—C≡\overset{\ominus\oplus}{C}Na \longrightarrow$ cycloalkyne $\xrightarrow[\text{Catalyst}]{\text{Lindlar}}$ *cis*-product(B)

(By acid-base reaction)

9. (b) $Ph—C≡C—H + MeO^{\ominus} \rightleftharpoons Ph—C≡C^{\ominus} + MeOH$ (St. acid)

equilibrium is backward. $\quad\therefore$ $MeO^{\ominus}$ will attack as a nucleophile

$$Ph—C≡C—H + Me\overset{\ominus}{O} \longrightarrow Ph—C^{\ominus}=CH—OMe \xrightarrow{H—O—Me} Ph—CH=CH—OMe$$

10. (d) $Ph—C(Cl)_2—CH_3 \xrightarrow{2NaNH_2} Ph—C\equiv CH \xrightarrow{NaNH_2} Ph—C\equiv C^{\ominus}Na^{\oplus}$ (A)

11. (b) $H—C(CH_3)(Et)—CH_2—CH_2—CH_2—Br \xrightarrow[-Br^{\ominus}]{\overset{\oplus}{Na}\overset{\ominus}{C}\equiv C} H—C(CH_3)(Et)—(CH_2)_3—C\equiv CH$

12. (d) Reaction proceed through enol format on and H_2O attack on stable carbocation in this reaction.

∴ (d) is most favourable. (Kucherov reaction)

13. (c) Acid-base reaction follower by S_{N^2}

∴ I is better leaving group than Br.

∴ (c) is favourable.

14. (c) $Ph—C\equiv C—H \xrightarrow{\text{(base)}} Ph—C\equiv \overset{\ominus}{C} + I-I \longrightarrow Ph—C\equiv C—I$

(base: morpholine, N—H)

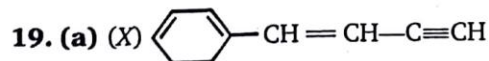
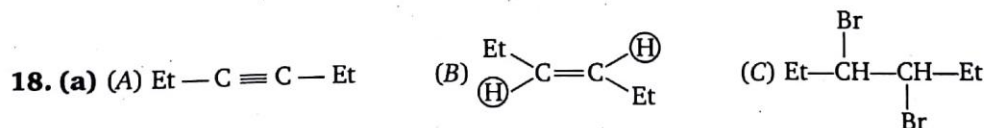
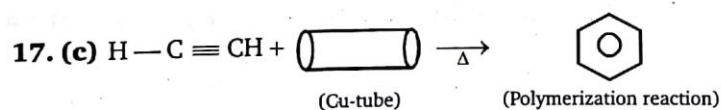
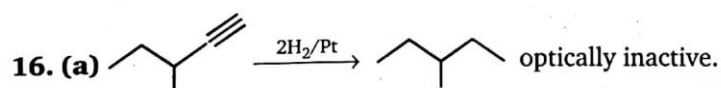
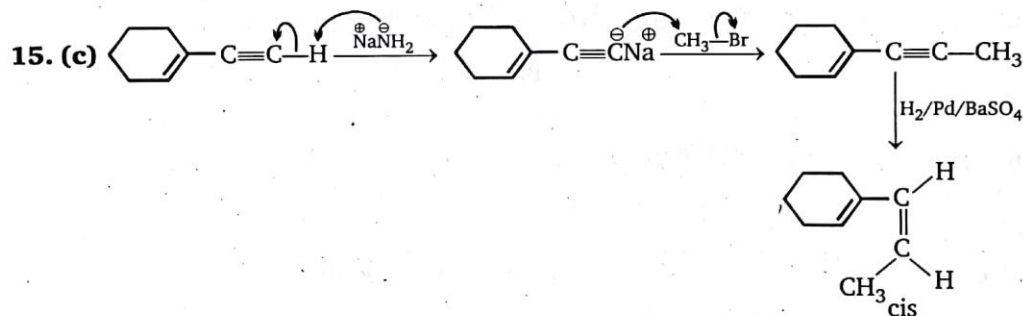
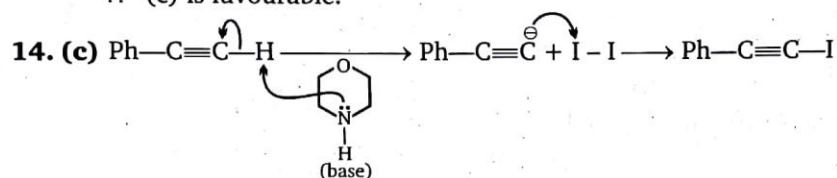
15. (c) (cyclohexenyl)—C≡C—H $\xrightarrow{\overset{\oplus}{Na}\overset{\ominus}{NH_2}}$ (cyclohexenyl)—$C\equiv\overset{\ominus}{C}\overset{\oplus}{Na}$ $\xrightarrow{CH_3—Br}$ (cyclohexenyl)—$C\equiv C—CH_3$ $\xrightarrow{H_2/Pd/BaSO_4}$ (cyclohexenyl)—CH=CH—CH_3 (cis)

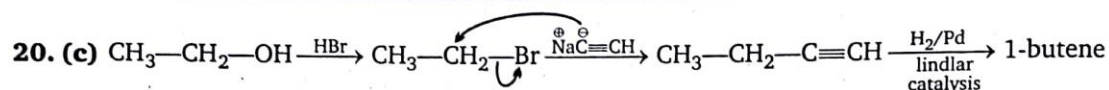
16. (a) (3-methylpent-1-yne) $\xrightarrow{2H_2/Pt}$ (3-methylpentane) optically inactive.

17. (c) $H—C\equiv CH$ + (Cu-tube) $\xrightarrow{\Delta}$ (benzene)

(Cu-tube) (Polymerization reaction)

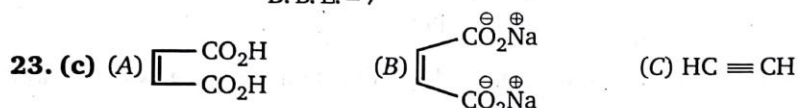
18. (a) (A) $Et—C\equiv C—Et$ (B) Et(H)C=C(H)Et (C) Et—CH(Br)—CH(Br)—Et

19. (a) (X) (Ph)—$CH=CH—C\equiv CH$

gives all the given products in different reaction.

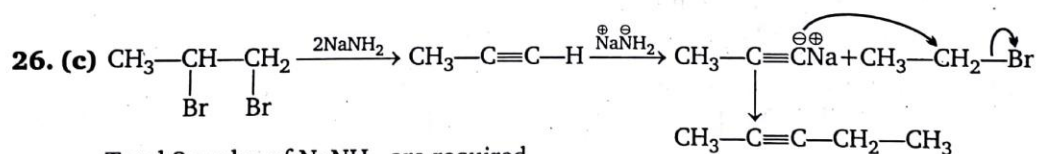
20. (c) $CH_3—CH_2—OH \xrightarrow{HBr} CH_3—CH_2—Br \xrightarrow{\overset{\oplus}{Na}\overset{\ominus}{C}\equiv CH} CH_3—CH_2—C\equiv CH \xrightarrow[\text{lindlar catalysis}]{H_2/Pd}$ 1-butene

21. (b) Symmetrical alkyne will give acid only. (*i.e.*, 4-octyne)

22. (c) Degree of unsaturation (or) Double bond equivalent $= (C+1) - \left(\frac{H+X-N}{2}\right)$

$$D.B.E. = 7$$

23. (c) (*A*) $HO_2C—CH=CH—CO_2H$ (*B*) $\overset{\ominus}{C}O_2\overset{\oplus}{Na}—CH=CH—\overset{\ominus}{C}O_2\overset{\oplus}{Na}$ (*C*) $HC\equiv CH$

24. (c) None of the given reagent.

25. (a) (*A*) $H—C\equiv C—CH_2—CH_3$ (Terminal alkyne gives white ppt. with ammonical $AgNO_3$)

26. (c) $CH_3—CH(Br)—CH_2(Br) \xrightarrow{2NaNH_2} CH_3—C\equiv C—H \xrightarrow{\overset{\oplus}{Na}\overset{\ominus}{N}H_2} CH_3—C\equiv \overset{\ominus}{C}\overset{\oplus}{Na} + CH_3—CH_2—Br \rightarrow CH_3—C\equiv C—CH_2—CH_3$

Total 3 moles of $NaNH_2$ are required.

27. (c) $CH_3—CH(CH_3)—C\equiv CH \xrightarrow{H^+Br^-} CH_3—CH(CH_3)—C(Br)=CH_2 \xrightarrow{H^+Br^-} CH_3—CH(CH_3)—C(Br)_2—CH_3$

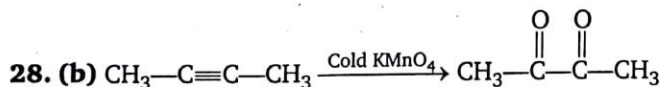
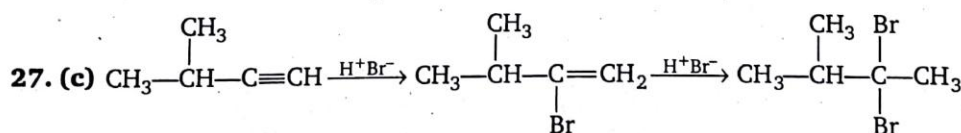
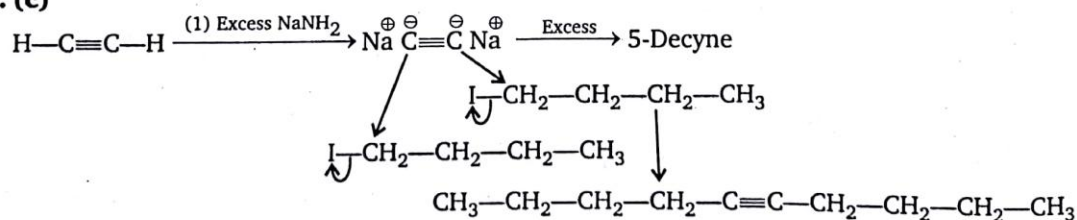
28. (b) $CH_3—C\equiv C—CH_3 \xrightarrow{\text{Cold } KMnO_4} CH_3—\overset{O}{\overset{\|}{C}}—\overset{O}{\overset{\|}{C}}—CH_3$

29. (d)

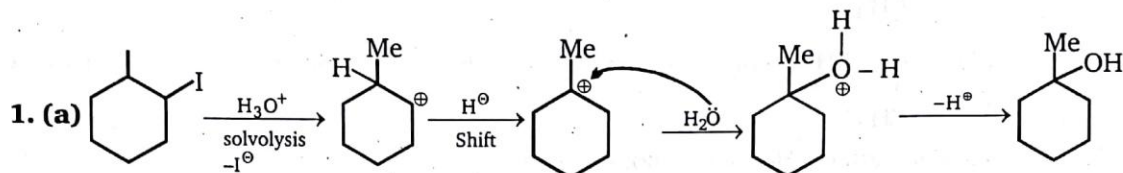
30. (c)

$H—C\equiv C—H \xrightarrow{(1)\text{ Excess } NaNH_2} \overset{\oplus}{Na}\overset{\ominus}{C}\equiv\overset{\ominus}{C}\overset{\oplus}{Na} \xrightarrow{\text{Excess}}$ 5-Decyne

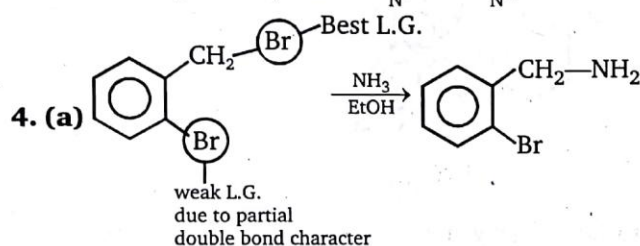
(with $I—CH_2—CH_2—CH_2—CH_3$ on each side)

$CH_3—CH_2—CH_2—CH_2—C\equiv C—CH_2—CH_2—CH_2—CH_3$

5(A) Alkyl Halides (Substitution Reaction)

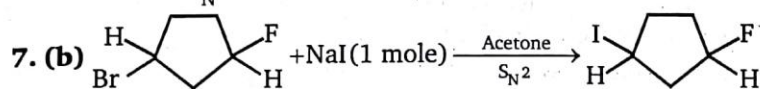
Level-1

1. (a)

2. (b) Inverted product on the carbon where leaving group is present.

3. (c) At bridge head position S_{N^1} and S_{N^2} do not takes place.

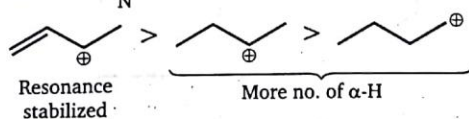
4. (a) o-Bromobenzyl bromide (CH_2–Br: Best L.G.; ring Br: weak L.G. due to partial double bond character) $\xrightarrow[EtOH]{NH_3}$ o-Bromobenzylamine (CH_2—NH_2, Br)

5. (b) S_{N^2} reaction is favourable at least crowded site.

6. (b) Rate of S_{N^2} = k [Substrate] [Nu^-]

7. (b) 1-Bromo-3-fluorocyclopentane (H, Br / F, H) + NaI (1 mole) $\xrightarrow[S_N2]{Acetone}$ (I, H / F, H)

Above reaction depends on L-G-tendency. $Br^{\ominus}$ is better leaving group than $F^{\ominus}$.

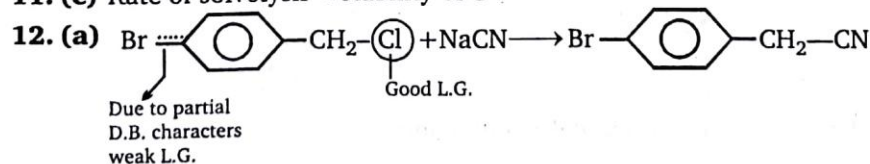
8. (d) Unstable $C^{\oplus}$ has general tendency to rearrange to more stable $C^{\oplus}$.

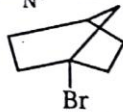
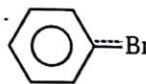
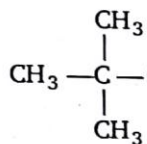
9. (b) Rate of S_{N^1} $\propto$ stability of $C^{\oplus}$ in R.D.S.

Allyl cation (Resonance stabilized) > secondary cation > primary cation (More no. of α-H)

10. (a) Rate of S_{N^2} $\propto \dfrac{1}{\text{Steric crowding near to reaction centre}}$

11. (c) Rate of solvolysis $\propto$ stability of $C^{\oplus}$

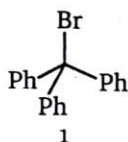
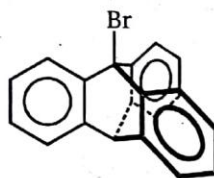
12. (a) Br–C_6H_4–CH_2–Cl + NaCN ⟶ Br–C_6H_4–CH_2—CN

(Br: Due to partial D.B. characters weak L.G.; Cl: Good L.G.)

13. (d) S_{N^1} and S_{N^2} not possible in the following.

Br

Stearically crowded reaction center for S_{N^2} Bridgehead $C^{\oplus}$ sp^2 hybridized not possible (Bredt's rule). Hence S_{N^1} and S_{N^2} not possible.

Br Lone pair of Br in resonance with Benzene ring. Hence partial double bond character. No S_{N^1} or S_{N^2} possible.

$CH_3-C(CH_3)_2-CH_2-Br$ 1° $C^{\oplus}$ not stable. Hence S_{N^1} not possible stearic crowded for backside attack. Hence S_{N^2} not possible.

14. (d) In 1-bromotriptycener,

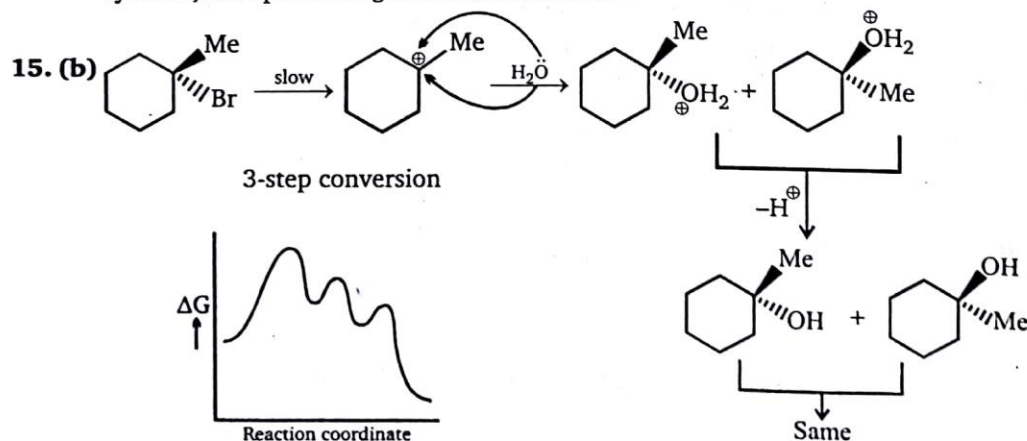
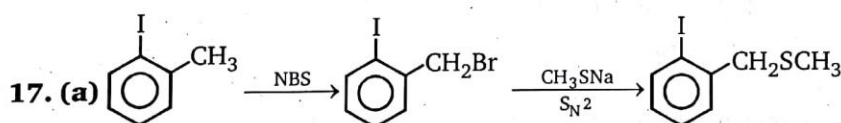
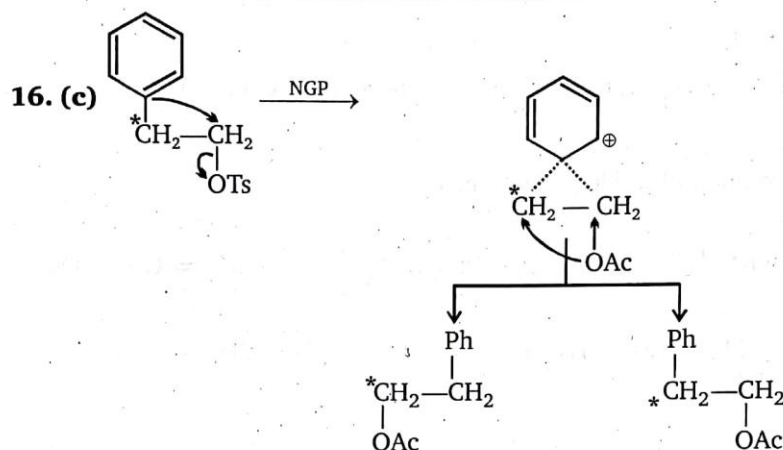
Br, Ph, Ph, Ph, 1 (I)

Br, 10^{-23} (II)

The bromine atom is found to be virtually inert to nucleophilies. Despite the formal resemblance in the environment of the bromine atom in to that in, they are found to differ in their rate of reaction under parallel conditions by a factor of $\approx 10^{-23}:1$! This is because stabilisation of the carbocation in (I) can occur by delocalisation of its charge through the π-orbital systems of the three benzene rings; whereas the extremely rigid structure of (II) will hold the cation's empty orbital (from loss of $Br^{\ominus}$) but at right angles to these π-orbital systems, thus preventing such delocalisation.

15. (b)

two intermediate formed carbocation & oxoniumion.

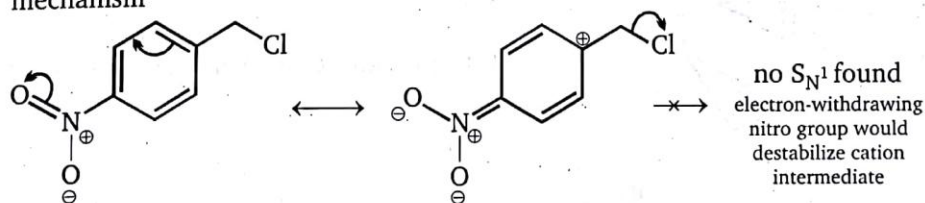
16. (c) $\overset{*}{C}H_2-CH_2-OTs$ (Ph on $\overset{*}{C}H_2$) $\xrightarrow{NGP}$ phenonium ion ($\overset{*}{C}H_2 - CH_2$ bridged), attacked by OAc →

Ph–$CH_2-\overset{*}{C}H_2$–OAc (i.e. $\overset{*}{C}H_2(OAc)-CH_2Ph$) and $\overset{*}{C}H_2(Ph)-CH_2-OAc$

17. (a) 2-iodotoluene (CH_3) $\xrightarrow{NBS}$ 2-iodobenzyl bromide (CH_2Br) $\xrightarrow[S_N2]{CH_3SNa}$ 2-iodobenzyl methyl sulfide (CH_2SCH_3)

NBS Brominates Allyl position only.

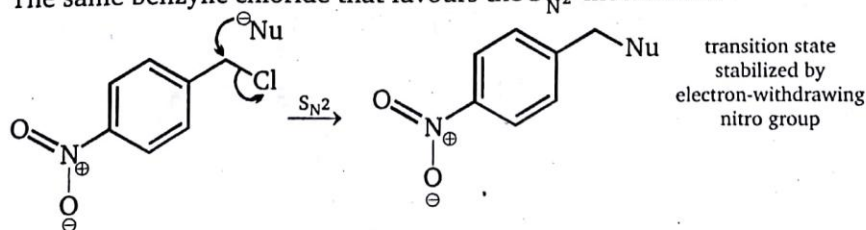
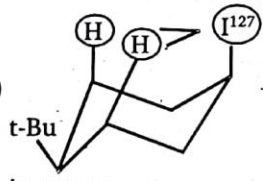
18. (a) Rate of $S_{N^2} \propto \frac{1}{\text{Steric crowding near to reaction centre}}$

19. (c) Rate of $S_{N^1} \propto$ stability of $C^{\oplus}$ in R.D.S.

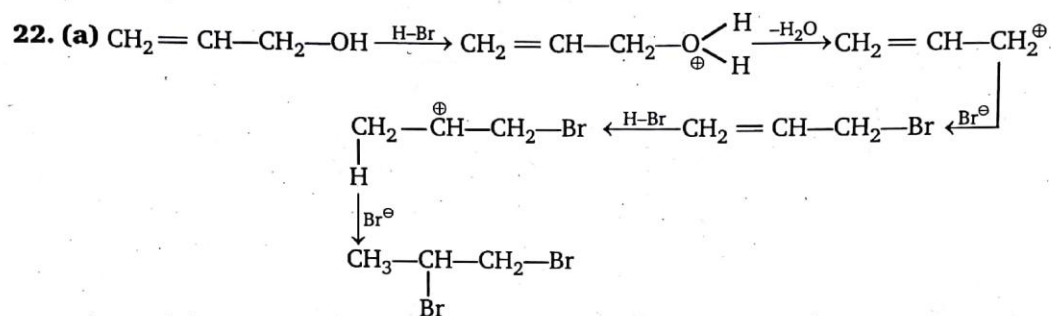
20. (d) On the other hand, a 4-nitrobenzyl chloride is likely to react by the S_{N^2} mechanism as the strongly electron-withdrawning nitro group would destabilize the carbocation intermediate of the S_{N^1} mechanism. a benzylic chloride that disfavours the S_{N^1} mechanism

no $S_N{}^1$ found
electron-withdrawing nitro group would destabilize cation intermediate

The same benzylic chloride that favours the S_{N^2} mechanism.

$\xrightarrow{S_N2}$ 4-nitrobenzyl–Nu

transition state stabilized by electron-withdrawing nitro group

21. (b) In $CH_3-C(CH_3)(Br)-CH_2-CH_3$ rate of reaction is faster than $CH_3-CH(Br)-CH(CH_3)-CH_3$ because in former compound stable $C^{\oplus}$ is formed.

22. (a) $CH_2=CH-CH_2-OH \xrightarrow{H-Br} CH_2=CH-CH_2-\overset{\oplus}{O}H_2 \xrightarrow{-H_2O} CH_2=CH-CH_2^{\oplus}$

$\xrightarrow{Br^{\ominus}} CH_2=CH-CH_2-Br \xrightarrow{H-Br} CH_2(H)-\overset{\oplus}{C}H-CH_2-Br \xrightarrow{Br^{\ominus}} CH_3-CH(Br)-CH_2-Br$

23. (c) In case of rearrangement S_{N^1} and S_{N^2} product are different.

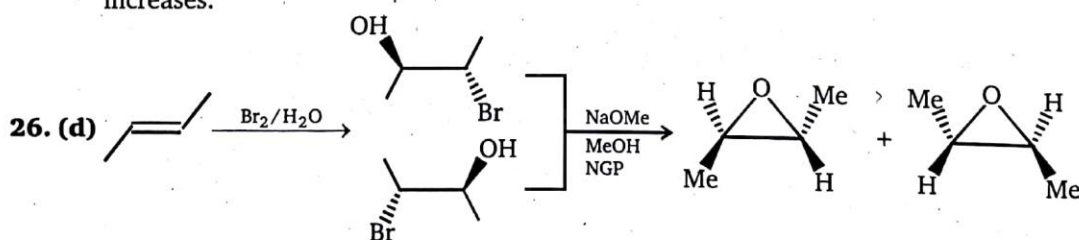
24. (c) (A) $Br^{\ominus}$ is best L.G. than $-O-\overset{O}{\overset{\|}{C}}-Me$

(B) $SH^{\ominus}$ is best $Nu^{\ominus}$ than MeSH

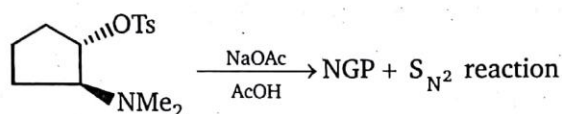
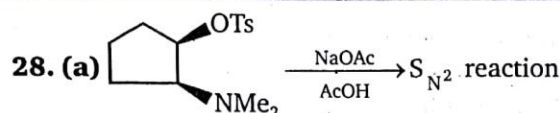
(C) $Cl^{\ominus}$ is best $Nu^{\ominus}$ than $I^{\ominus}$ in DMSO

(D) In polar protic solvent $I^{\ominus}$ is better $Nu^{\ominus}$ than $Cl^{\ominus}$

25. (d) [Chair cyclohexane with t-Bu, axial H, H and I^{127}] $\longrightarrow$ due to 1,3 repulsion L.G. tendency increases so rate of reaction increases.

26. (d) [but-2-ene] $\xrightarrow{Br_2/H_2O}$ [bromohydrins: OH/Br] $\xrightarrow{\text{NaOMe, MeOH, NGP}}$ [epoxide: H, Me, Me, H] + [epoxide: Me, H, H, Me]

27. (d) In polar protic solvent, less hydrogen bonding nucleophile is more nucleophilic.

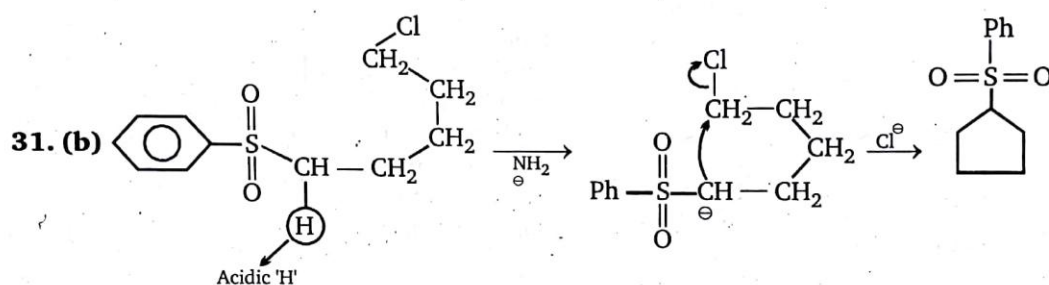
28. (a) OTs, NMe_2 (cis) $\xrightarrow[AcOH]{NaOAc}$ S_{N^2} reaction

OTs, NMe_2 (trans) $\xrightarrow[AcOH]{NaOAc}$ NGP + S_{N^2} reaction

29. (a) Rate of $S_{N^1} \propto C^{\oplus}$ stability

Rate of $S_{N^2} \propto \frac{1}{\text{steric crowding around reaction centre}}$

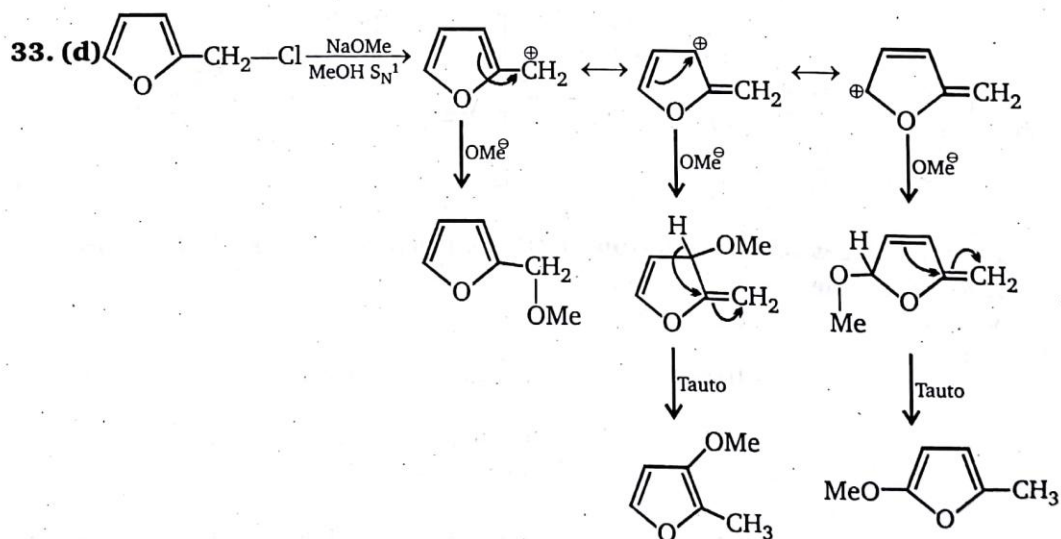
30. (d) Consider nucleophilicity order.

31. (b) $C_6H_5-SO_2-CH(H)-CH_2-CH_2-CH_2-CH_2Cl$ $\xrightarrow{\overset{\ominus}{NH_2}}$ $Ph-SO_2-\overset{\ominus}{C}H-CH_2-CH_2-CH_2-CH_2-Cl$ $\xrightarrow{Cl^{\ominus}}$ cyclopentyl phenyl sulfone ($O=S(Ph)=O$)

Acidic 'H'

32. (d) In the reaction, formation of a π-bond, Elimination.

33. (d) Furan$-CH_2-Cl$ $\xrightarrow[MeOH\ S_{N^1}]{NaOMe}$ Furan$-\overset{\oplus}{C}H_2$ ⟷ (ring $\oplus$)$=CH_2$ ⟷ $\oplus$(ring)$=CH_2$

$\downarrow OMe^{\ominus}$: Furan$-CH_2-OMe$; H, OMe ring adduct $=CH_2$; $H(MeO)$ ring adduct $=CH_2$

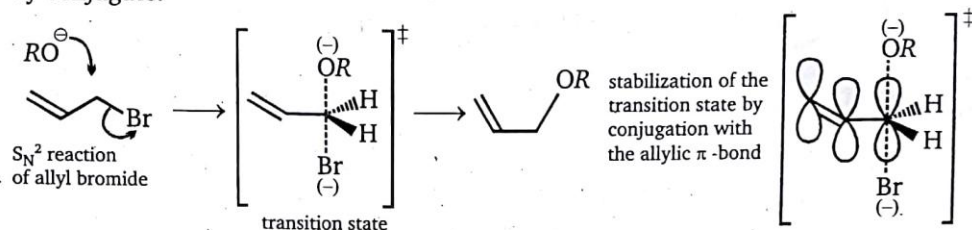
$\downarrow$ Tauto : 3-methoxy-2-methylfuran (OMe, CH_3); MeO–furan–CH_3

34. (c) Br is best L.G. and inversion of configuration takes place in S_{N^2}.

35. **A-a, B-b** In S_{N^2}, T.S. will be more stable, means more rate.

36. (d) Here you see a typical $S_{N}2$ reaction of allyl bromide. We have drawn the transition state for this reaction. This is not because we want to encourage you to do this for all S_N2 reactions but so that we can explain the role of the allyl system. Allyl compounds react rapidly by the $S_{N}2$ mechanism because the double bond can stabilize the transitions state by conjugate.

S_N2 reaction of allyl bromide

transition state

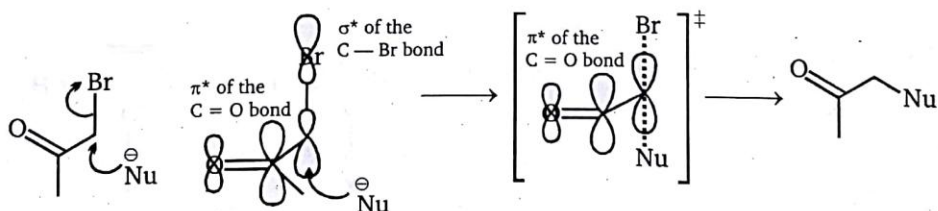
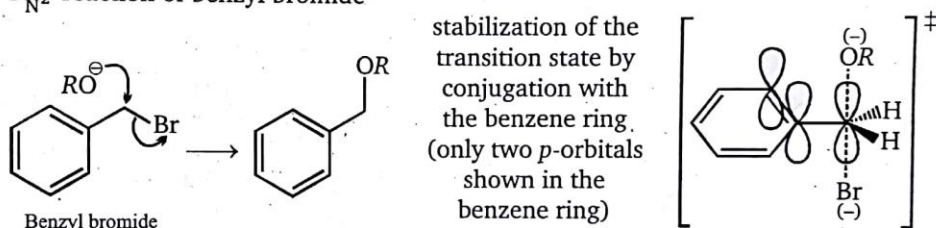
stabilization of the transition state by conjugation with the allylic π-bond

The benzyl group acts in much the same way using the π system of the benzene ring for conjugation with the *p*-orbital in the transition state.

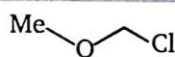
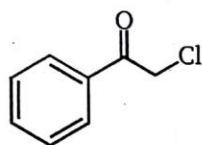
$S_{N}2$ reaction of benzyl bromide

Benzyl bromide

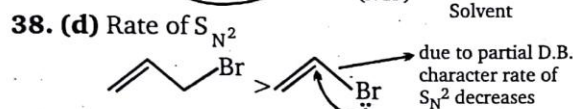
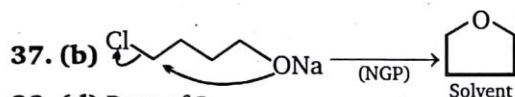
stabilization of the transition state by conjugation with the benzene ring (only two *p*-orbitals shown in the benzene ring)

σ* of the C — Br bond

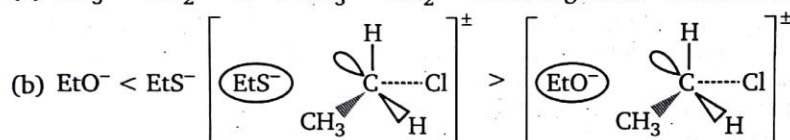
π* of the C = O bond

Relative rates of $S_{N}2$ reaction of alkyl chlorides with the iodide ion

Alkyl chloride	**Relative rate**	**Comments**
Me — Cl	200	Least hindered alkyl chloride
(isopropyl chloride)	0.02	Secondary alkyl chloride; slow because of steric hinderance
(allyl chloride)	79	allyl chloride accelerated by π conjugation in transition state
(benzyl chloride)	200	benzyl chloride slightly more reactive than allyl: benzene ring better at π conjugation than isolated double bond

Me–O–CH₂–Cl	920	conjugation with oxygen lone pair accelerates reaction
PhCOCH₂Cl	100000	conjugation with carbonyl group much more effective than with simple alkene or benzene ring. These α-carbonyl halides are the most reactive of all

37. (b) Cl–CH₂CH₂CH₂CH₂–ONa $\xrightarrow{\text{(NGP)}}$ (tetrahydrofuran) Solvent

38. (d) Rate of $S_{N}2$

$CH_2=CH-CH_2-Br$ > $CH_2=CH-Br$ → due to partial D.B. character rate of S_N2 decreases

39. $EtS^{\ominus}$ is more nucleophilic than $EtO^{\ominus}$

(a) $CH_3-CH_2-O^- > CH_3-CH_2-OH$ charged Nu^- better than neutral.

(b) $EtO^- < EtS^-$ $\left[(EtS^-) \cdots C(H)(CH_3)(H) \cdots Cl \right]^{\pm}$ > $\left[(EtO^-) \cdots C(H)(CH_3)(H) \cdots Cl \right]^{\pm}$

More stable T.S. because of more bonding due to large size.

(c) Rate of $S_{N}2$ α [Substrate] $[Nu^-]$

It is equal for both 1 and 2.

(d) $Ph_3P > Ph_3N$

$Et-\overset{\oplus}{P}Ph_3 > Et-\overset{\oplus}{N}Ph_3$ more stable because more charge dispersion on larger atom.

40. (d) $S_{N}1$ reaction depends on :

(1) Leaving group tendency

(2) Conc. of substrate

(3) Dielectric constant of solvent.

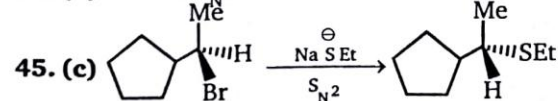
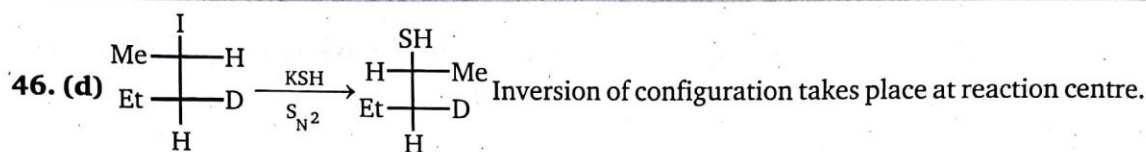
41. (d) For $S_{N}2$ order w.r.t. Nu is 1 & order w.r.t. substrate is one if reaction increases 10 times when conc. of (Nu) increases 10 times.

42. (a) Rate of $S_{N}2$ $= K$ [Substrate] [Nu]

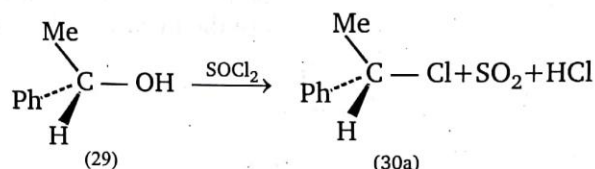
43. (c) Rate of $S_{N}2$ $= K$ [Substrate] [Nu]

44. (b) Rate of $S_{N}2$ $= K$ [Substrate] [Nu]

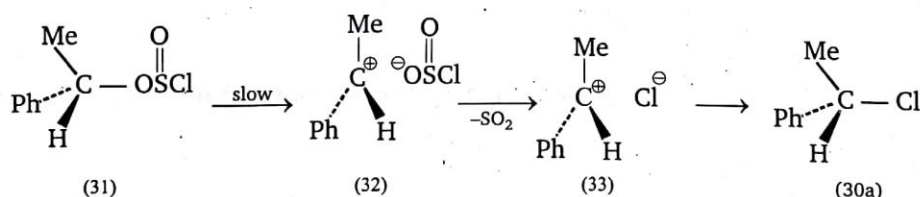
45. (c) Cyclopentyl–C(Me)(H)(Br) $\xrightarrow[S_N2]{Na\overset{\ominus}{S}Et}$ Cyclopentyl–C(Me)(SEt)(H)

46. (d) Me–C(I)(H)–, Et–C(D)(H) $\xrightarrow[S_N2]{KSH}$ H–C(SH)(Me), Et–C(D)(H) Inversion of configuration takes place at reaction centre.

47. (a) $S_{N}1$ mechanism: retention of configuration:

Retention of configuration, means the starting material and product have the same configuration.

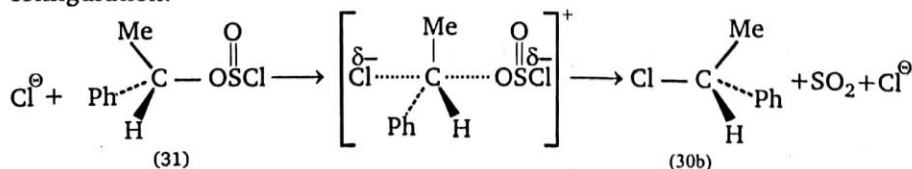
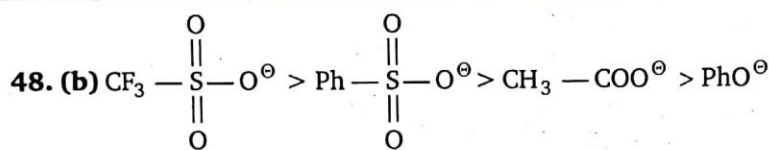
$$\text{Ph(Me)(H)C–OH (29)} \xrightarrow{SOCl_2} \text{Ph(Me)(H)C–Cl (30a)} + SO_2 + HCl$$

The reaction has been shown to follow a second order rate equation rate $= k_2$ [*R*OH][$SOCl_2$], but clearly cannot proceed by the simple S_N2 mode for this would lead to inversion of configuration in the product, which is not observed.

Carrying out the reaction under milder conditions allows of the isolation of an alkyl chlorosulphite, *R*OSOCl (31), and this can be shown to be a true intermediate. The chlorosulphite is formed with retention of configuration, the *R*–O bond not being broken during the reaction. The rate at which the alkyl chlorosulphite intermediate (31) breaks down to the product, *R*Cl (30a), is found to increase with increasing polarity of the solvent, and also with increasing stability of the carbocation $R^{\oplus}$: an ion pair, $R^{\oplus}$ $^{\ominus}$OSOCl (32), is almost certainly involved. Provided collapse of the ion pair to products then occurs rapidly, *i.e.*, in the intimate ion pair (33) within a solvent cage, then attack by $Cl^{\ominus}$ is likely to occur on the same side of $R^{\oplus}$ from which $^{\ominus}$OSOCl departed, *i.e.*, with retention of configuration:

$$\text{Ph(Me)(H)C–OS(=O)Cl (31)} \xrightarrow{slow} \text{Ph(Me)(H)C}^{\oplus}\ ^{\ominus}\text{OS(=O)Cl (32)} \xrightarrow{-SO_2} \text{Ph(Me)(H)C}^{\oplus}\ Cl^{\ominus} \text{ (33)} \longrightarrow \text{Ph(Me)(H)C–Cl (30a)}$$

Whether the breaking of the C—O and the S—Cl bonds occurs simultaneously, or whether the former occurs first, is still a matter of debate.

It is interesting that if the $SOCl_2$ reaction on *R*OH (29) is carried out in the presence of pyridine, the product *R*Cl is found now to have undergone inversion of configuration (30b). This occurs because the HCl produced during the formation of (31) from *R*OH and $SOCl_2$ is converted by pyridine into $C_5H_5NH^{\oplus}$ $Cl^{\ominus}$ and $Cl^{\ominus}$, being an effective nucleophile, attacks (31) 'from the back' in a normal S_N2 reaction with inversion of configuration:

$$Cl^{\ominus} + \text{Ph(Me)(H)C–OS(=O)Cl (31)} \longrightarrow \left[\overset{\delta-}{Cl}\cdots\text{C(Me)(Ph)(H)}\cdots\text{OS(=O)}\overset{\delta-}{Cl}\right]^{+} \longrightarrow \text{Cl–C(Me)(H)Ph (30b)} + SO_2 + Cl^{\ominus}$$

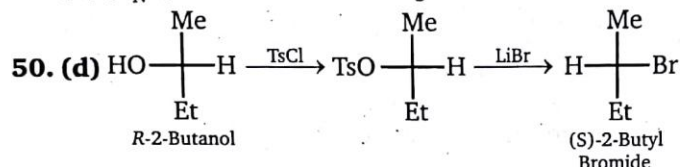
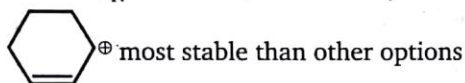
48. (b) $CF_3-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-O^{\ominus} > Ph-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-O^{\ominus} > CH_3-COO^{\ominus} > PhO^{\ominus}$

L.G. Ability

49. (b) $(S_N2) \rightarrow$ Inversion of configuration at reaction centre.

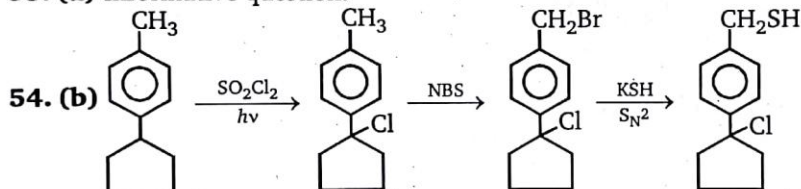
50. (d) HO–C(Me)(Et)–H $\xrightarrow{TsCl}$ TsO–C(Me)(Et)–H $\xrightarrow{LiBr}$ H–C(Me)(Et)–Br

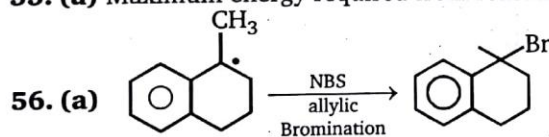
R-2-Butanol (S)-2-Butyl Bromide

51. (b) Rate of $S_{Ni} \propto$ stability of $C^{\oplus}$

(cyclohexenyl cation) most stable than other options

52. (d) Because of good leaving group.

53. (a) Informative question.

54. (b)

55. (a) Maximum energy required from reactant, is known as rate determining step (R.D.S.).

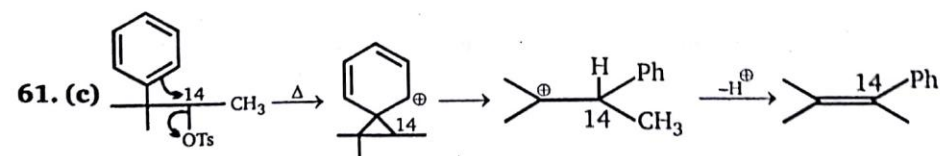
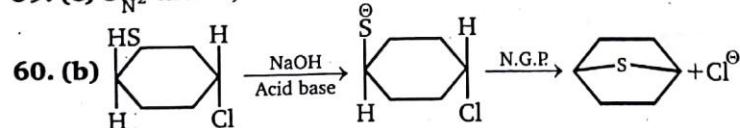
56. (a) $\xrightarrow[\text{Bromination}]{\text{NBS, allylic}}$ (CH$_3$, Br product)

Stable radical due to resonance and hyper conjugation

57. (b) S_{N2} take place, at less steric site.

58. (c) If same atom then, Nucleophilicity $\propto$ Basicity.

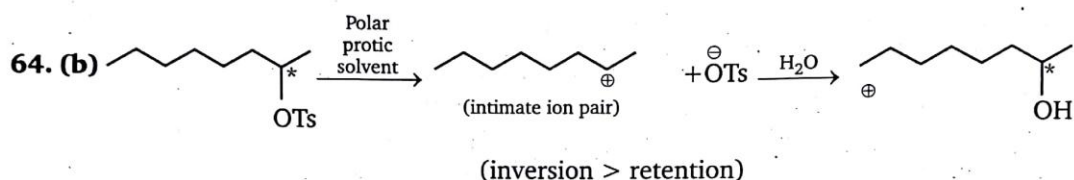
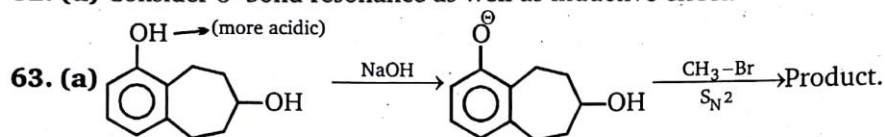
59. (c) S_{N2} means, inversion.

60. (b) $\xrightarrow[\text{Acid base}]{\text{NaOH}}$ $\xrightarrow{\text{N.G.P.}}$ $+Cl^{\ominus}$

61. (c) $\xrightarrow{\Delta}$ $\longrightarrow$ $\xrightarrow{-H^{\oplus}}$

62. (d) Consider σ-bond resonance as well as inductive effect.

63. (a) OH → (more acidic); —OH $\xrightarrow{NaOH}$ $O^{\ominus}$ —OH $\xrightarrow[S_N2]{CH_3-Br}$ Product.

64. (b) OTs $\xrightarrow{\text{Polar protic solvent}}$ $\oplus$ (intimate ion pair) $+\overset{\ominus}{O}Ts$ $\xrightarrow{H_2O}$ $\oplus$ OH

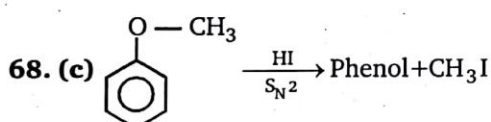
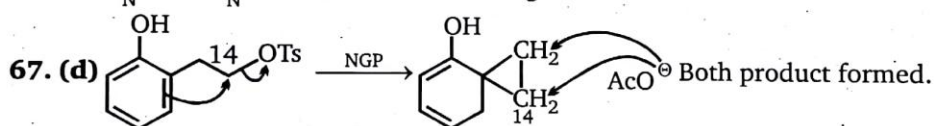
(inversion > retention)

∴ (*S*)-2 octanol > (*R*)-2 octanol

65. (c) (B) Less steric – Favour for S_{N^2}

(A) Good leaving group – Favour for S_{N^2}

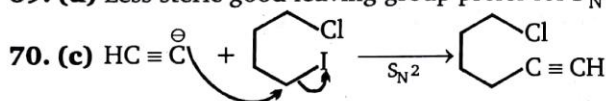
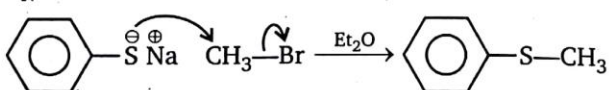
66. (c) S_{N^2} and S_{N^1} same, if $C^{\oplus}$ not rearrange.

67. (d) OH, 14 OTs $\xrightarrow{NGP}$ OH, CH_2, CH_2 14, $AcO^{\ominus}$ Both product formed.

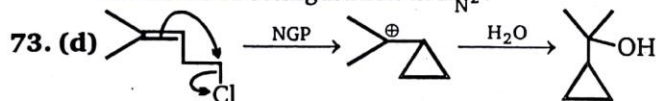
68. (c) O — CH_3 $\xrightarrow[S_N2]{HI}$ Phenol+CH_3I

69. (d) Less steric good leaving group prefer for S_{N^2}.

70. (c) $HC\equiv\overset{\ominus}{C}$ + Cl, I $\xrightarrow{S_N2}$ Cl, $C\equiv CH$

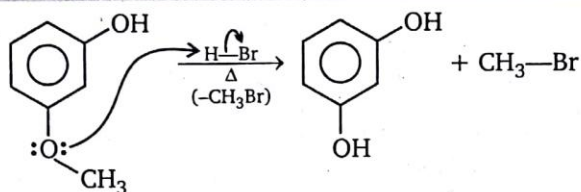
71. (c) S_{N^2}

$\overset{\ominus}{S}\overset{\oplus}{Na}$ CH_3—Br $\xrightarrow{Et_2O}$ S—CH_3

72. (b) One interchange.

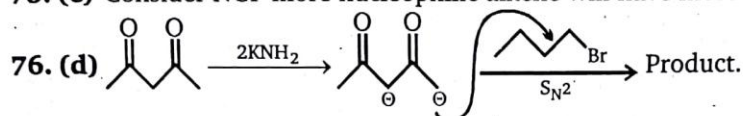
Inversion of configuration in S_{N^2}.

73. (d) Cl $\xrightarrow{NGP}$ $\oplus$ $\xrightarrow{H_2O}$ OH

74. (b) (*A*) ⟶ S_{N^1} (*B*) ⟶ S_{N^2}

(*A*) ⟶ S_{N^1} because highly stable $C^{\oplus}$ is formed.

OH, :O:–CH_3 $\xrightarrow[\Delta \; (-CH_3Br)]{H—Br}$ OH, OH + CH_3—Br

No L.G. Hence l.p. on oxygen will act as $Nu^{\ominus}$.

75. (c) Consider NGP more nucleophilic alkene will have more rate of reaction.

76. (d) $\xrightarrow{2KNH_2}$ $\xrightarrow[S_N2]{Br}$ Product.

Prefer less steric nucleophile.

(1° carbanion>2° carbanion) order of nucleophilicity (less steric hindered is more nucleophilic)

77. (b) (*A*) ⊕, Anti-aromatic intermediate.

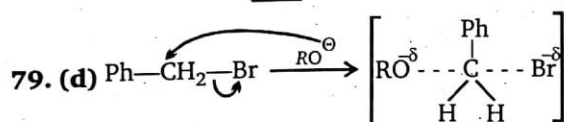
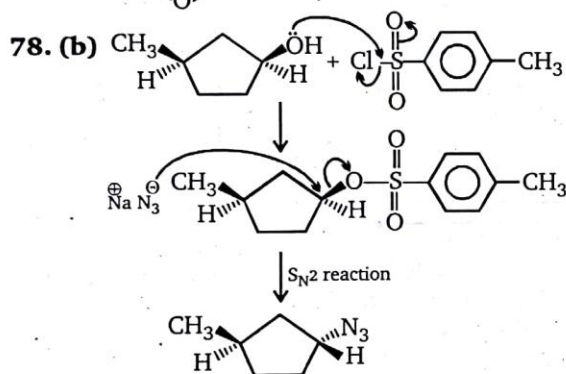
(*B*) ⊕ O, Aromatic intermediate.

78. (b) CH_3, H, ÖH, H + Cl–S(=O)(=O)–C$_6$H$_4$–CH_3

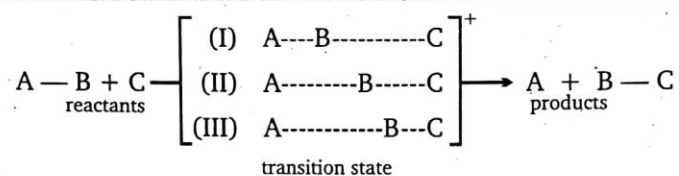
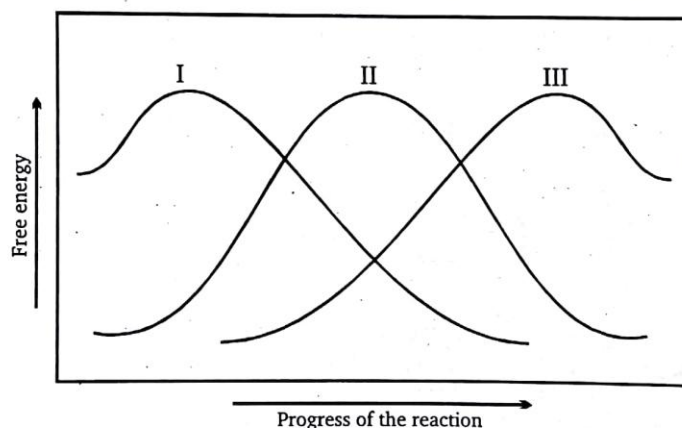
$\overset{\oplus}{Na}\overset{\ominus}{N_3}$ CH_3, H, O–S(=O)(=O)–C$_6$H$_4$–CH_3, H

S_N2 reaction

CH_3, H, N_3, H

79. (d) Ph—CH_2—Br $\xrightarrow{RO^{\ominus}}$ $\left[\overset{-\delta}{RO} - - - \underset{H \;\; H}{\overset{Ph}{C}} - - - \overset{-\delta}{Br} \right]$

80. (b) Replacement of Br by OH so nucleophilic substituion.

81. (c) Knowing something about the structure of a transition state is important when you are trying to predict the products of a reaction. The structure of the transition state lies between the structure of the reactants and the structure of the products. But what do we mean by "between"? Does the structure of the transition state lie exactly halfway between the structures of the reactants and products (as in II, below), or does it resemble the reactants more closely than it resembles the products (as in I), or is it more like the products than the reactants (as in III)?

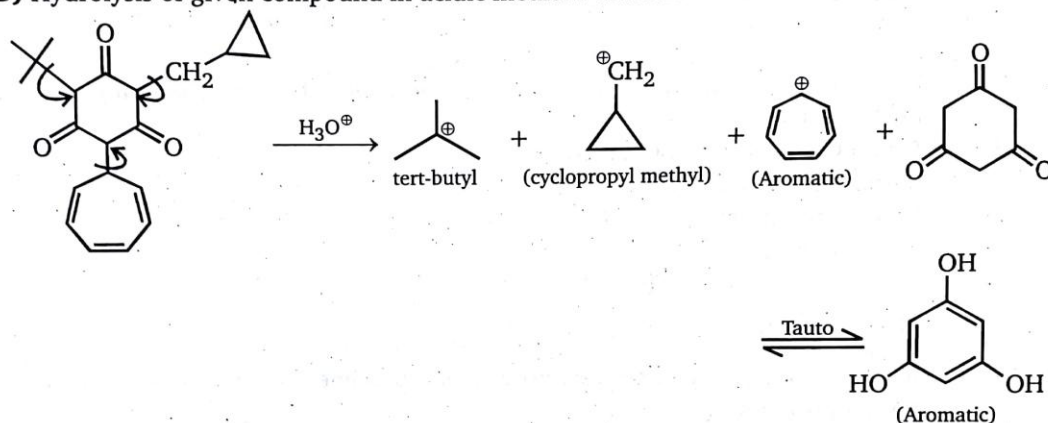
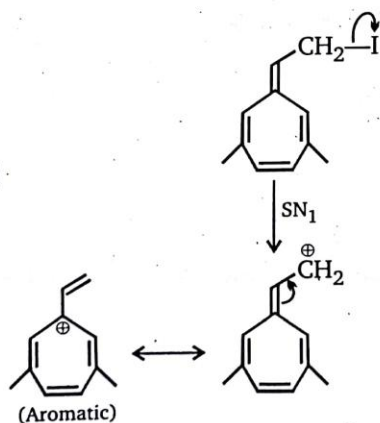
$$\underset{\text{reactants}}{A-B+C} \longrightarrow \underset{\text{transition state}}{\begin{bmatrix} \text{(I)} & A\text{---}B\text{-----------}C \\ \text{(II)} & A\text{---------}B\text{------}C \\ \text{(III)} & A\text{-----------}B\text{---}C \end{bmatrix}^{+}} \longrightarrow \underset{\text{products}}{A + \dot{B}-C}$$

According to the Hammond postulate, the transition state will be more similar in structure to the species that it is more similar to in energy. In the case of an exergonic reaction, the transition state is more similar in energy to the reactant than to the product. (curve I). Therefore, the structure of the transition state will more closely resemble the structure of the reactant than that of the transition state will more closely resemble the structure of the reactant than that of the product. In an endergonic reaction (curve III), the transition state is more similar in energy to the product, so the structure of the transition state will more closely resemble the structure of the product. Only when the reactant and the product have identical energies (curve II) would we expect the structure of the transition state to be halfway between the structures of the reactant and the product.

Now we can understand why the tert-butyl cation is formed faster than the isobutyl cation when 2-methylpropene reacts with HCl. Of the two possible products, the tert-butyl cation (a tertiary carbocation) is more stable than the isobutyl cation (a primary carbocation). Because formation of a carbocation is an endergonic reaction, the structure of the transition state will resemble the structure of the carbocation product. This means that the transition state will have a significant amount of positive charge on a carbon. The same factors that stabilize the positively charged product will stabilize the partially positively charged transition state. Therefore, the transition state leading to the tert-butyl cation is more stable than the transition state leading to the isobutyl cation, so the tert-butyl cation will be formed faster. It is important to keep in mind that the amount of positive charge in the transition state is not as great as the amount of positive charge in the transition state is not as great as the amount of positive charge in the carbocation product, so the difference in the stabilities of the two transition states is not as great as the difference in the stabilities of the two carbocation products.

82. (b) Hydrolysis of given compound in acidic medium will form well-known stable cations.

$\xrightarrow{H_3O^{\oplus}}$ tert-butyl + (cyclopropyl methyl) + (Aromatic) + ... $\xrightleftharpoons{\text{Tauto}}$ (Aromatic)

83. (c)

84. (d)

CH_2—I $\xrightarrow{SN_1}$ $\overset{\oplus}{C}H_2$ ⟷ (Aromatic)

Level-2

1. In polar protic solvent, $I^{\ominus}$ is less stable due to less hydrogen bonding it means more nucleophilic.

2. Acetone is polar aprotic solvent.

3. Basic information.

4. Basic information.

5. Basic information.

6. For $S_{N^1} \Rightarrow 3^o > 2^o > 1^o$

For $S_{N^2} \Rightarrow 3^o < 2^o < 1^o$

7. At Bridge head halide and resonance stablized halide do not show S_{N^1} and S_{N^2}.

8. Basic information.

9. (1) Good leaving group (2) Polar protic solvent (3) Less steric reactant

10. Basic information.

11. (A) Polar aprotic solvent favour S_{N^2}

(B) Polar protic solvent favour S_{N^1}, elimination is not possible.

(C) E_2 methoxide amine is a strong base.

(D) Polar protic solvent favour S_{N^1}

(E) $CN^{\ominus}$ is a good nucleophile so S_{N^2}

(F) $CN^{\ominus}$ is a good nucleophile so S_{N^2}

(G) $Br^{\ominus}$ (48%) it means nucleophile is available for S_{N^2}.

12. (A) S_{N^2} favour if 1^o & 2^o alkyl halide are available except vinyl, aryl, neopentyl, bridgehead halide.

(B) If β-hydrogens are available then E_2 possible.

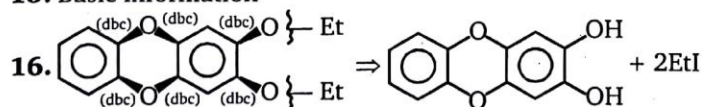
(C) Aryl, neopentyl and bridgehead halide do not show S_{N^1}, S_{N^2}, E_1 E_2

13. (1) (A) Reaction faster due to 3^o R – I

(2) (D) More reactive due to S_{N^2} reaction

(3) (E) More reactive due to S_{N^2} reaction

(4) (G) More reactive due to good leaving group.

(5) (I) More reactive due to resonance stablized transition state formed.

14. 3, Anyl, neopentyl, bridge head halide do not show S_{N^2}.

15. Basic information

16. (dbc) (dbc) (dbc) O – Et / (dbc) (dbc) (dbc) O – Et $\Rightarrow$ OH / OH + 2EtI

17. a = P,r ; b = q ; c = s ; d = r

(a) Ph–C(Cl) $\xrightarrow[\text{(Polar protic solvent)}]{H_2O}$ Ph–C$^{\oplus}$ + $Cl^{\ominus}$ (SN_1) Carbocation is intermediate

(b) $\xrightarrow[SN_2]{Ph-S^{\ominus}Na^{\oplus}}$ SPh $+ Cl^{\ominus}$

(c) $\xrightarrow[Ar\text{-}SN]{K\overset{\ominus}{O}H}$ F, $\ominus$OH, NO_2 (carbanion intermediate)

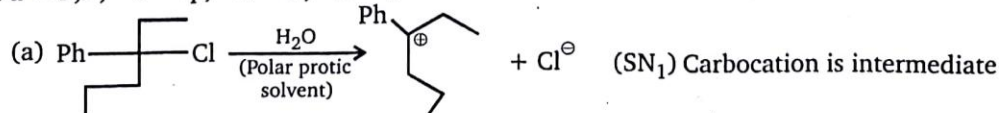
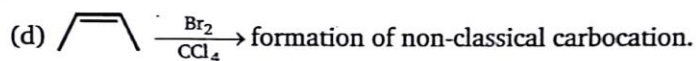
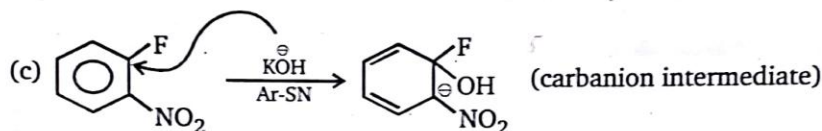
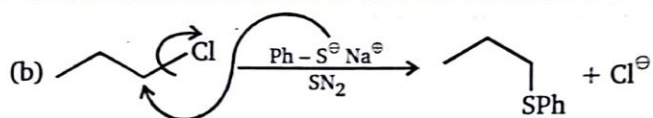
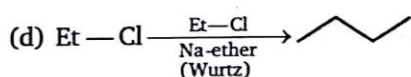
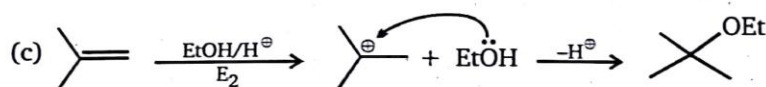
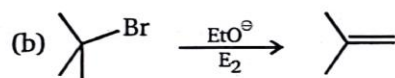
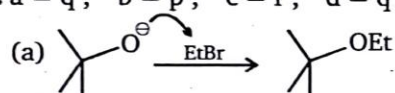
(d) $\xrightarrow[CCl_4]{Br_2}$ formation of non-classical carbocation.

18. a = q ; b = p ; c = r ; d = q

(a) $O^{\ominus}$ $\xrightarrow{EtBr}$ OEt

(b) Br $\xrightarrow[E_2]{EtO^{\ominus}}$

(c) $\xrightarrow[E_2]{EtOH/H^{\oplus}}$ $\oplus$ + EtÖH $\xrightarrow{-H^{\oplus}}$ OEt

(d) Et — Cl $\xrightarrow[\text{Na-ether (Wurtz)}]{Et—Cl}$

19. a = p ; b = r ; c = s ; d = q

(a) Substitution takes place in only compound (1). In compound (4), HBr will be eliminated hence elimination reaction, not substitution. Hence compound (1).

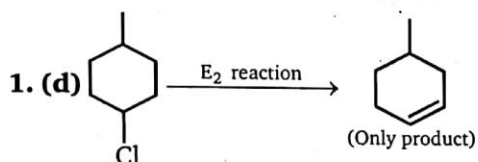
(b) Williamson ether synthesis ⇒ substitution can not take place on benzene hence compound (3).

(c) Aq. ethanol will substitute Br^- with EtO^- and H^+ ions released in the solution turning the solution acidic in compound (4) Hence compound (4).

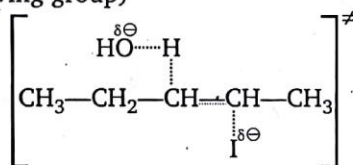
(d) In compound (3), after cleavage, positive charge will be on benzene ring which is highly unstable. Hence compound (2).

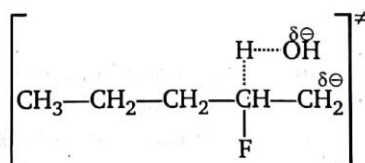
5(B) Alkyl Halides (Elimination Reaction)

Level-1

1. (d)

2. **A–a ; B–d**

In case of good leaving group (reaction proceed through stable transition state stability of T.S. by alkene ($I^{\ominus}$ good leaving group)

$$\left[\begin{array}{c} \overset{\delta\ominus}{HO}\cdots H \\ CH_3-CH_2-CH \cdots CH-CH_3 \\ \overset{\delta\ominus}{I} \end{array}\right]^{\neq}$$

If leaving group is strong base reaction proceed through stable carbanion in transition state.

$$\left[\begin{array}{c} H\cdots\overset{\delta\ominus}{OH} \\ CH_3-CH_2-CH_2-CH-\overset{\delta\ominus}{CH_2} \\ F \end{array}\right]^{\neq}$$

carbanion is more stable. ∴Hoffmann product is major.

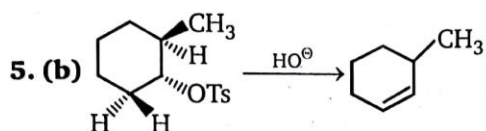
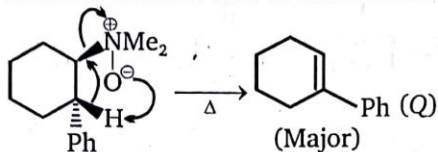
3. (a) 2 amine, 2 times Hoffmann exhaustive methylation.

Two times Methylation; Methylation

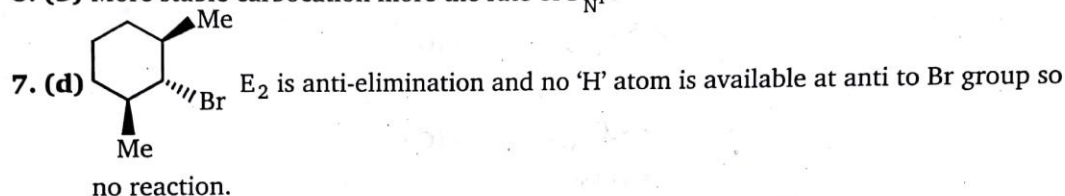
4. (c) $\longrightarrow$ (*P*), (in cope elimination, syn-elimination, hydrogen and $\overset{\ominus}{O}-\overset{\oplus}{N}Me_2$

must be on same side so that reaction proceed through cyclic transition steps.

$\overset{\oplus}{N}Me_2$, $O^{\ominus}$, H, Ph $\xrightarrow{\Delta}$ Ph (Q) (Major)

5. (b) CH_3, H, OTs, H, H $\xrightarrow{HO^{\ominus}}$ CH_3

(Anti-elimination take place in E_2 reaction)

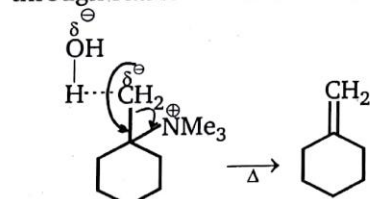
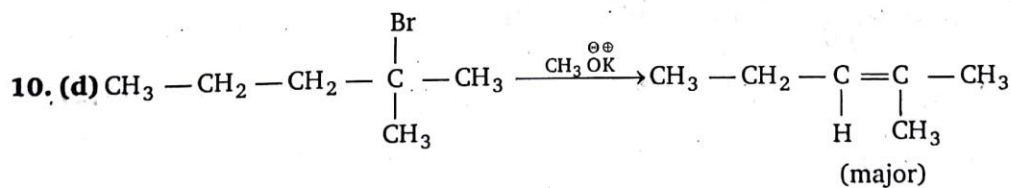
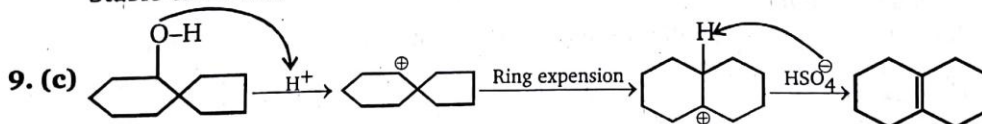
6. (b) More stable carbocation more the rate of S_{N^1}.

7. (d) Me, Br, Me E_2 is anti-elimination and no 'H' atom is available at anti to Br group so no reaction.

8. (b) Hoffmann elimination take place because of poor leaving $-\overset{\oplus}{N}Me_3$, reaction proceed through stable carbanion in transition state. Hoffmann elimination is major.

$\xrightarrow{\Delta}$ CH_2

Stable carbanion

9. (c) O–H $\xrightarrow{H^+}$ ⊕ $\xrightarrow{\text{Ring expension}}$ H, ⊕ $\xrightarrow{HSO_4^{\ominus}}$

10. (d) $CH_3-CH_2-CH_2-\underset{CH_3}{\overset{Br}{C}}-CH_3 \xrightarrow{CH_3\overset{\ominus\oplus}{OK}} CH_3-CH_2-\underset{H}{C}=\underset{CH_3}{C}-CH_3$ (major)

11. (c) Anti-elimination takes place.

12. (c) E_2 reaction.

13. (c) Br, Br $\xrightarrow{Zn}$ $\overset{\ominus}{}$ZnBr, Br $\longrightarrow$ △ + $ZnBr_2$

14. (d) (*A*) O, OH Tauto (*B*) O, OH Tauto (*C*) O, OH Tauto

(Phenol will obtained)

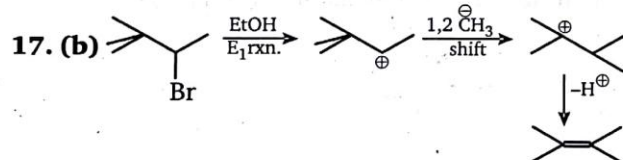
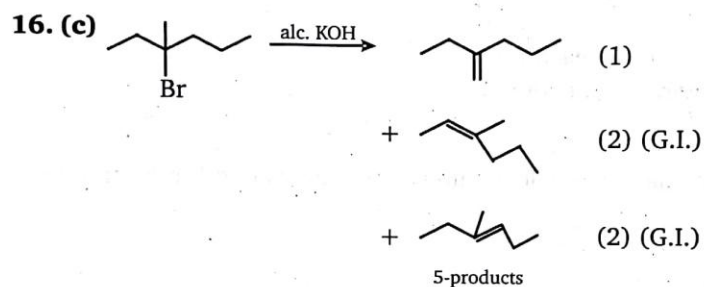
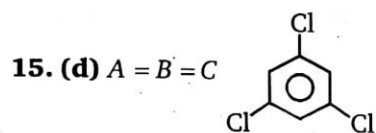
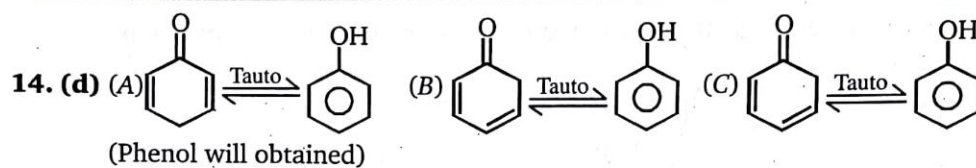
15. (d) $A = B = C$ Cl, Cl, Cl

16. (c) Br alc. KOH (1)

+ (2) (G.I.)

+ (2) (G.I.)

5-products

17. (b) Br EtOH E_1 rxn. ⊕ 1,2 $\overset{\ominus}{C}H_3$ shift ⊕ $-H^{\oplus}$

18. (b) At β-position –*M* gp. prefer elimination.

19. (c) Hoffmann elimination.

More number of β — H will give major product or Hoffmann elimination.

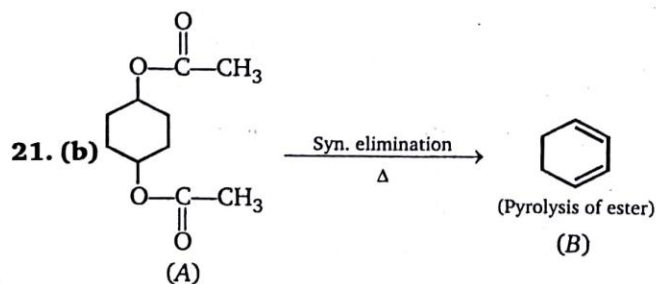
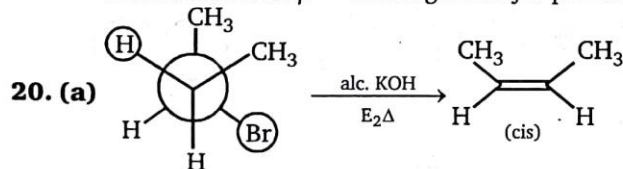
20. (a) CH_3, (H), CH_3, H, (Br), H alc. KOH $E_2\Delta$ CH_3 CH_3 H H (cis)

21. (b) O—C(=O)—CH_3, O—C(=O)—CH_3 Syn. elimination Δ

(*A*)

(Pyrolysis of ester)

(*B*)

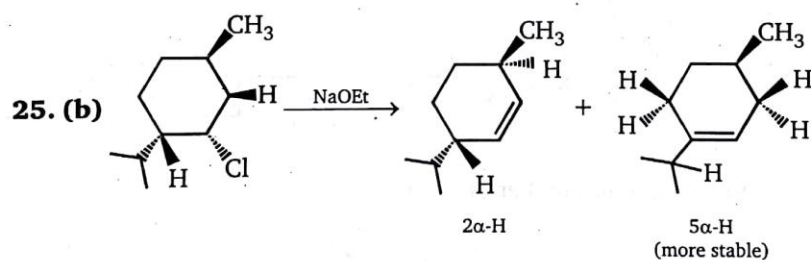
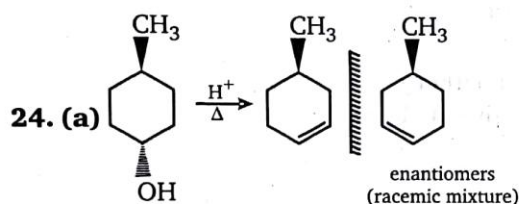
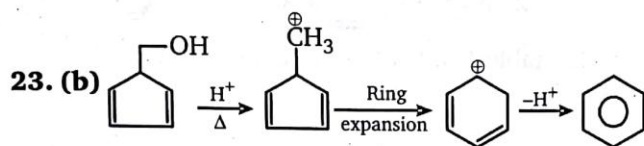
22. (a) $CH_3-CH(CH_3)-CH_2-\overset{\oplus}{N}(CH_3)_2-CH_2-CH_2-CH_3 \xrightarrow{\Delta} H_3C-CH=CH_2,$

Hoffmann alkene major product, because 2° carbanion is more stable than 3° carbanion.

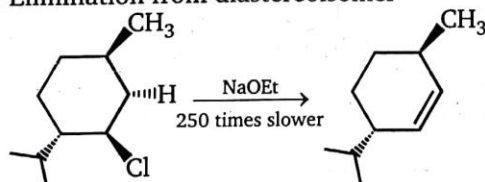
23. (b) $\xrightarrow[\Delta]{H^+}$ $\overset{\oplus}{C}H_2$ $\xrightarrow{\text{Ring expansion}}$ $\xrightarrow{-H^+}$

24. (a) $\xrightarrow[\Delta]{H^+}$

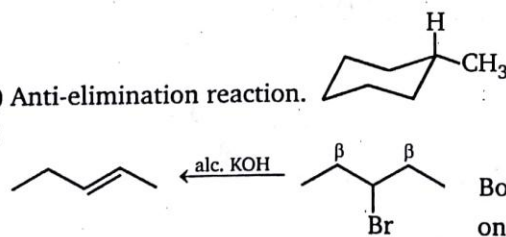
enantiomers (racemic mixture)

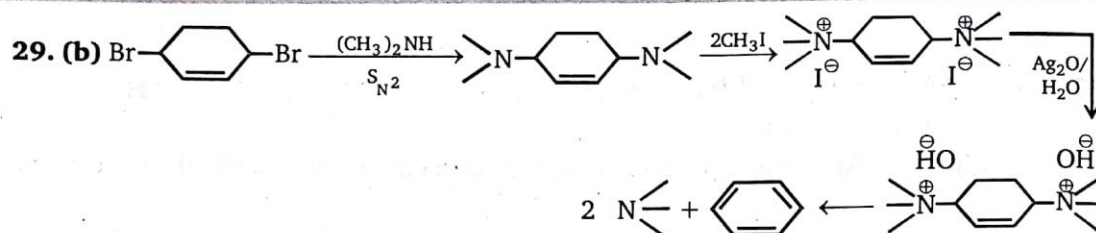
25. (b) $\xrightarrow{NaOEt}$ +

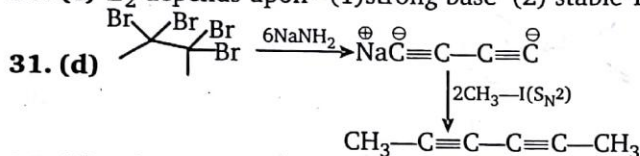
2α-H   5α-H (more stable)

26. (a) Elimination from diastereoisomer

$\xrightarrow[\text{250 times slower}]{NaOEt}$

27. (d) Anti-elimination reaction.

28. (c)

$\xleftarrow{\text{alc. KOH}}$ β β Br

Both β-positions have identical hydrogen and give only one product.

29. (b) Br–C₆H₈–Br $\xrightarrow[S_N2]{(CH_3)_2NH}$ $(CH_3)_2N$–C₆H₈–$N(CH_3)_2$ $\xrightarrow{2CH_3I}$ $(CH_3)_3\overset{\oplus}{N}$–C₆H₈–$\overset{\oplus}{N}(CH_3)_3$ $2I^{\ominus}$ $\xrightarrow{Ag_2O/H_2O}$ $(CH_3)_3\overset{\oplus}{N}$–C₆H₈–$\overset{\oplus}{N}(CH_3)_3$ $2\overset{\ominus}{O}H$ ⟶ 2 $N(CH_3)_3$ + benzene

30. (c) E_2 depends upon –(1)strong base (2) stable T.S. (3) leaving group ability.

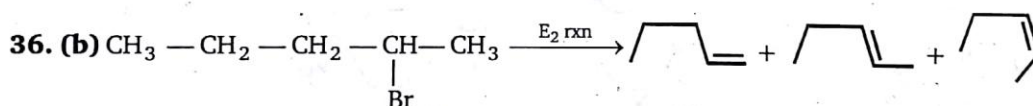
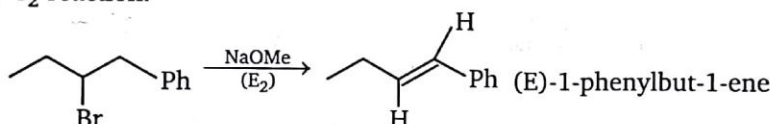
31. (d) $CH_3CBr_2CBr_2CH_3$ $\xrightarrow{6NaNH_2}$ $Na\overset{\oplus}{}\overset{\ominus}{C}\equiv C—C\equiv\overset{\ominus}{C}$ $\xrightarrow{2CH_3—I(S_N2)}$ $CH_3—C\equiv C—C\equiv C—CH_3$

32. (d) Informative question.

33. (a) (*A*)– Anti-elimination (*B*) Syn-elimination

34. (a) Dehydration followed by Hoffmann exhaustive methylation.

35. (a) E_2 reaction.

$CH_3CH_2CHBrCH_2Ph$ $\xrightarrow[(E_2)]{NaOMe}$ $CH_3CH_2CH=CHPh$ (E)-1-phenylbut-1-ene

36. (b) $CH_3—CH_2—CH_2—\underset{Br}{CH}—CH_3$ $\xrightarrow{E_2\ rxn}$ 1-pentene + trans-2-pentene + cis-2-pentene

Complex mixture means maximum number of alkene.

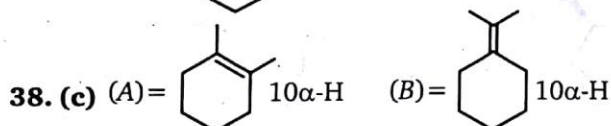
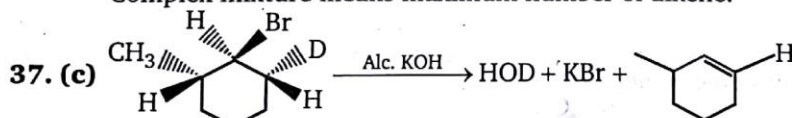
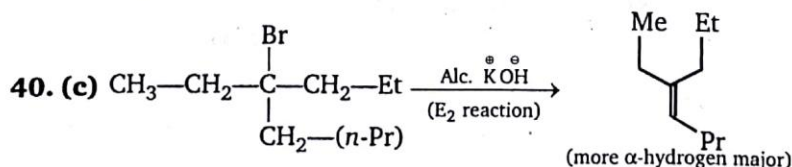
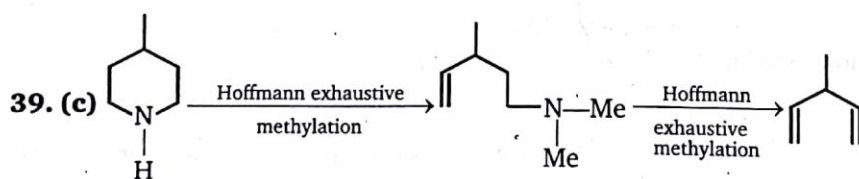
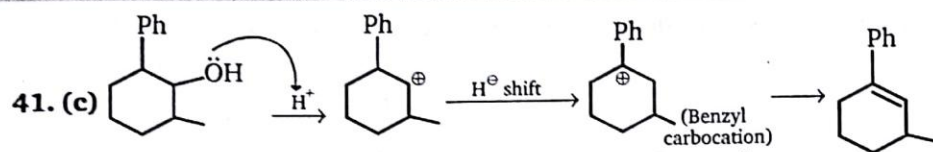
37. (c) (substituted cyclohexane with CH_3, H, Br, D, H) $\xrightarrow{Alc.\ KOH}$ HOD + KBr + 3-methylcyclohexene

38. (c) (*A*) = 1,2-dimethylcyclohexene 10α-H (*B*) = isopropylidenecyclohexane 10α-H

$$\boxed{A + B = 10 + 10 = 20\alpha\text{-H}}$$

39. (c) 4-methylpiperidine (N–H) $\xrightarrow{\text{Hoffmann exhaustive methylation}}$ $CH_2=CH–CH(CH_3)–CH_2CH_2–N(Me)–Me$ $\xrightarrow{\text{Hoffmann exhaustive methylation}}$ $CH_2=CH–CH(CH_3)–CH=CH_2$

40. (c) $CH_3—CH_2—\underset{CH_2—(n\text{-}Pr)}{\overset{Br}{C}}—CH_2—Et$ $\xrightarrow[(E_2\ reaction)]{Alc.\ \overset{\oplus}{K}\overset{\ominus}{O}H}$ (alkene with Me, Et, Pr substituents)
(more α-hydrogen major)

41. (c) Ph, ÖH; H^+; $H^\ominus$ shift; (Benzyl carbocation)

because of resonance and 3 α-H , this is the major product

42. (b) Br, Br, O; $NaOCH_3$(2 mole); H^+; O—H; OH; H; 1,2-hydride shift; OH; O; O—H

43. (b) $Zn \longrightarrow Zn^{+2} + 2e^{\ominus}$, $2e^{\ominus} + Ph—CH(Br)—CH_2—CH_2(Br) \longrightarrow Ph—\overset{\ominus}{C}H—CH_2—CH_2(Br)$

NGP (Neighbouring group participation)

Ph—cyclopropane

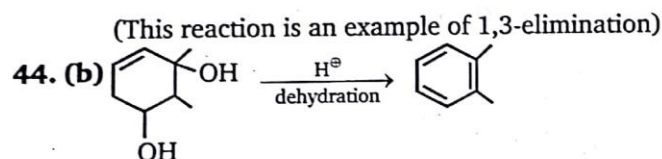
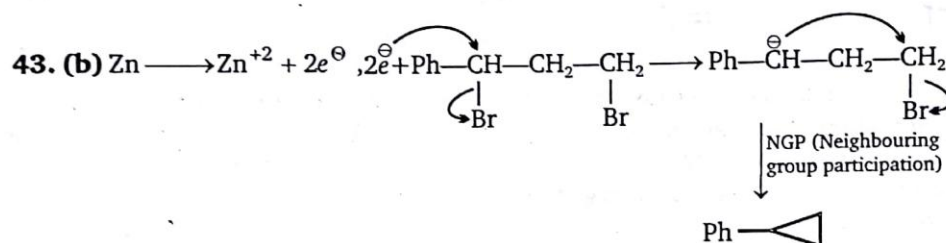
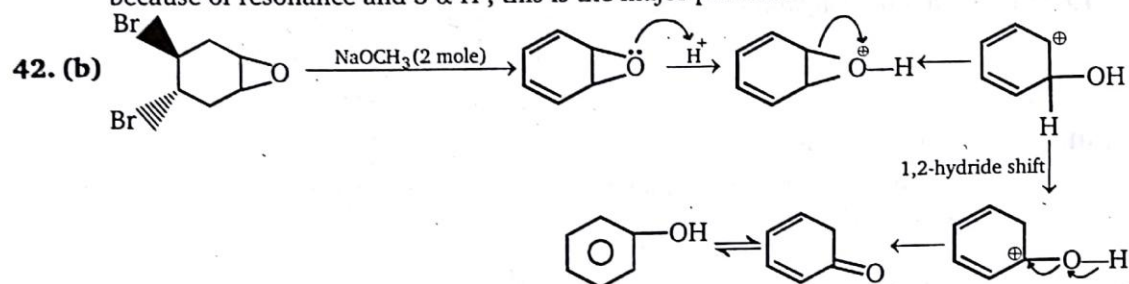
(This reaction is an example of 1,3-elimination)

44. (b) OH, OH; $H^{\oplus}$ dehydration

45. (c) Trans elimination.

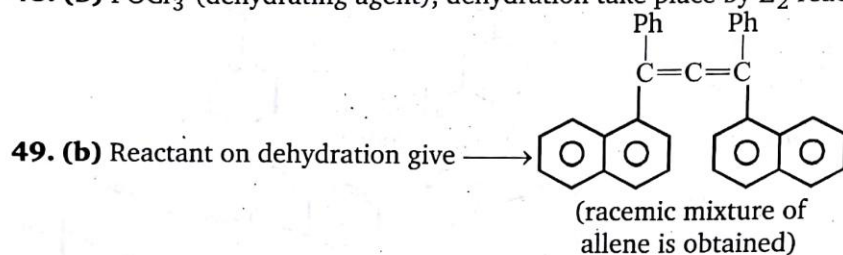
46. (a) N—N, Ph, H; $\overset{\ominus}{N}(i\text{-}Ph)_2$; N—N, Ph; $N{=}N—CH_2—\overset{\ominus}{C}H—Ph$; $HN(i\text{-}Ph)_2$; $+N_2+Ph—CH{=}CH_2$

(removal of good leaving group N_2 is driving force)

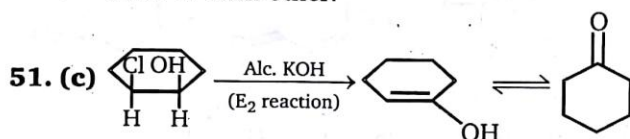
47. (d) NH; (1)CH_3I (excess) (2)moist Ag_2O; CH_3, CH_2—H, $\oplus$N, CH_3; $HO^\ominus$; Δ; N—Me, Me $+H_2C{=}CH_2$

48. (b) $POCl_3$ (dehydrating agent), dehydration take place by E_2 reaction.

49. (b) Reactant on dehydration give ⟶

Ph Ph
C=C=C

(racemic mixture of allene is obtained)

50. (a) ⟶ Trans elimination

EtO⁻ will bring about E_2 elimination of the reactant. Hence we want groups which are trans to each other.

51. (c) Cl OH, H H $\xrightarrow[(E_2 \text{ reaction})]{\text{Alc. KOH}}$ OH ⇌ O

NGP does not take place because chlorine and hydroxy group are on same side.

52. (b) In E_2 anti-elimination take place, H and bromine must be anti to each other (c) is most favourable because both hydrogen are anti to bromine most favourable for E_2 reaction. (b) is least reactive because hydrogen and bromine both are on same side. (b) is inert toward E_2 reaction.

53. (b) In presence of pair leaving group such as (fluorine), reaction proceed through stable carbanion in transition state.

$\overset{\delta\ominus}{B}$·······H
δ⊕
(B ⟶ base) Ph—CH—CH—CH₃ (F on second CH)

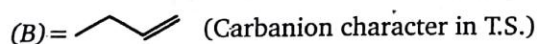
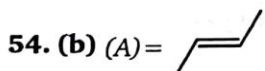
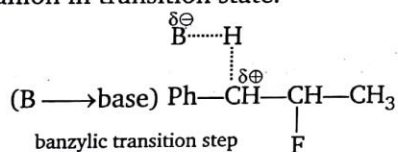
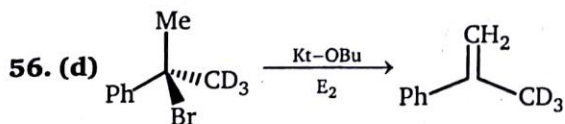
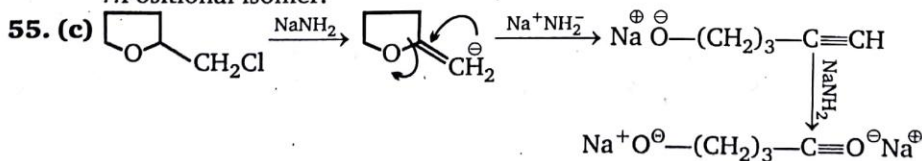
banzylic transition step

54. (b) *(A)* =

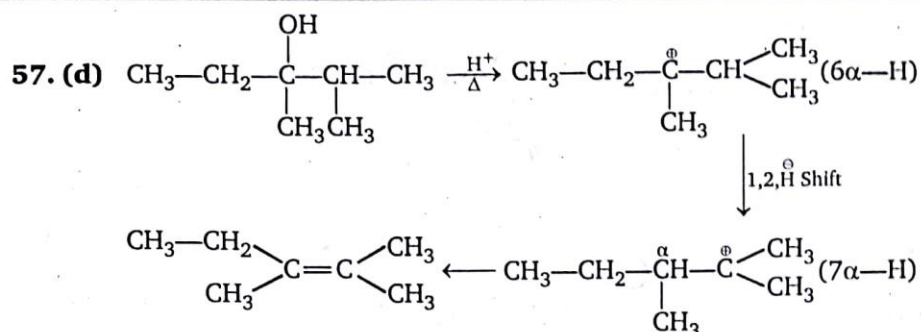
(B) = (Carbanion character in T.S.)

∴Positional isomer.

55. (c) CH_2Cl $\xrightarrow{NaNH_2}$ $\overset{\ominus}{C}H_2$ $\xrightarrow{Na^+NH_2^-}$ $\overset{\oplus}{Na}\,\overset{\ominus}{O}—(CH_2)_3—C{\equiv}CH$ $\xrightarrow{NaNH_2}$ $Na^+O^{\ominus}—(CH_2)_3—C{\equiv}C^{\ominus}Na^{\oplus}$

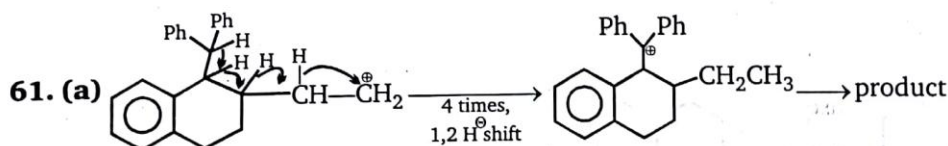
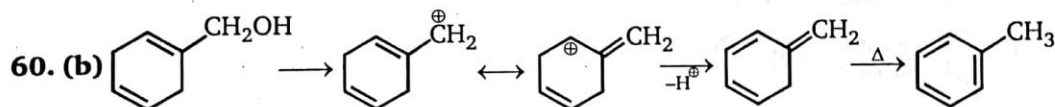
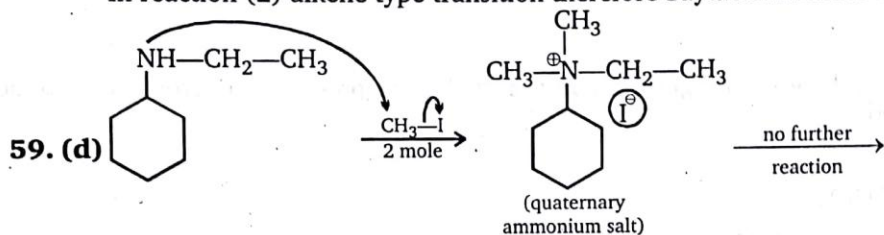
56. (d) Me, Ph, CD_3, Br $\xrightarrow[E_2]{\text{Kt–OBu}}$ CH_2, Ph, CD_3

Loss of chirality takes place during reaction.

57. (d) $CH_3—CH_2—C(OH)(CH_3)—CH(CH_3)—CH_3 \xrightarrow[\Delta]{H^+} CH_3—CH_2—\overset{\oplus}{C}(CH_3)—CH(CH_3)_2$ (6α—H)

$\xrightarrow{1,2,\overset{\ominus}{H}\text{ Shift}} CH_3—CH_2—\overset{\alpha}{C}H(CH_3)—\overset{\oplus}{C}(CH_3)_2$ (7α—H) $\longrightarrow (CH_3—CH_2)(CH_3)C{=}C(CH_3)_2$

58. (b) In reaction (1) carbanion type transition therefore Hoffmann alkene is major.
In reaction (2) alkene type transition therefore Saytzeff alkene is major.

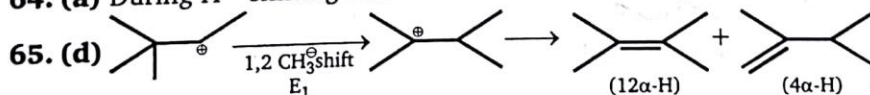
59. (d) Cyclohexyl–NH—CH$_2$—CH$_3$ $\xrightarrow[\text{2 mole}]{CH_3—I}$ Cyclohexyl–$CH_3—\overset{\oplus}{N}(CH_3)—CH_2—CH_3$ $I^{\ominus}$ (quaternary ammonium salt) $\xrightarrow[\text{reaction}]{\text{no further}}$

60. (b) (cyclohexadienyl)–CH_2OH $\longrightarrow$ (cyclohexadienyl)–$\overset{\oplus}{C}H_2$ $\longleftrightarrow$ ($\oplus$ ring)=CH_2 $\xrightarrow{-H^{\oplus}}$ (ring)=CH_2 $\xrightarrow{\Delta}$ (benzene)–CH_3

61. (a) (tetralin)–C(Ph)(Ph)H ... $\overset{|}{C}H—\overset{\oplus}{C}H_2$ $\xrightarrow[\text{1,2 }\overset{\ominus}{H}\text{ shift}]{\text{4 times,}}$ (tetralin with $\overset{\oplus}{C}$(Ph)(Ph))–CH_2CH_3 $\longrightarrow$ product

62. (b) For each carbocation rearrangement there must be some driving force.
Carbocation rearranges only when more stable carbocation is formed.

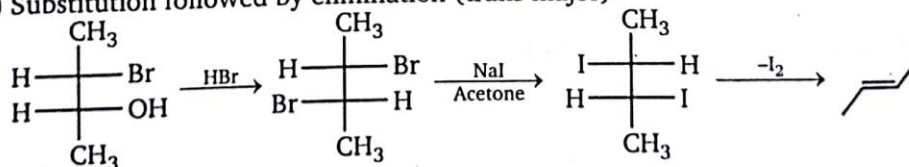
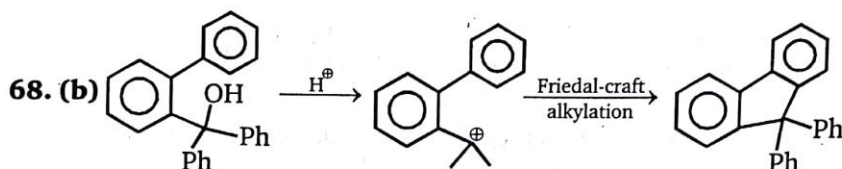
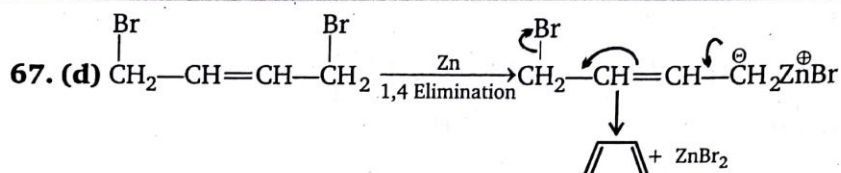
63. (d) Carbocation rearrange towards more stable carbocation.

64. (a) During $H^{\ominus}$ shifting carbon skeleton do not change.

65. (d) (carbocation) $\xrightarrow[E_1]{1,2\ CH_3^{\ominus}\text{shift}}$ (rearranged carbocation) $\longrightarrow$ (alkene) (12α-H) + (alkene) (4α-H)

66. (b) Substitution followed by elimination (trans major)

CH_3–CH(H)(Br)–CH(H)(OH)–CH_3 $\xrightarrow{HBr}$ CH_3–C(H)(Br)–C(Br)(H)–CH_3 $\xrightarrow[\text{Acetone}]{NaI}$ CH_3–C(I)(H)–C(H)(I)–CH_3 $\xrightarrow{-I_2}$ trans-2-butene

67. (d) $\underset{Br}{CH_2}-CH=CH-\underset{Br}{CH_2} \xrightarrow[\text{1,4 Elimination}]{Zn} \underset{Br}{CH_2}-CH=CH-\overset{\ominus}{CH_2}\overset{\oplus}{Zn}Br \rightarrow$ butadiene $+ ZnBr_2$

68. (b) $\xrightarrow{H^{\oplus}}$ $\xrightarrow{\text{Friedal-craft alkylation}}$ Ph, Ph

69. (b) Pinacol-Pinacolone rearrangment is an intramolecular process. ∴ no crossover products are obtained.

70. (a,b)

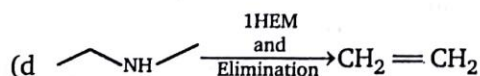
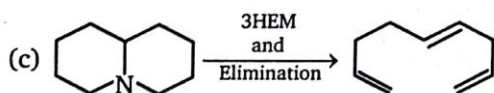
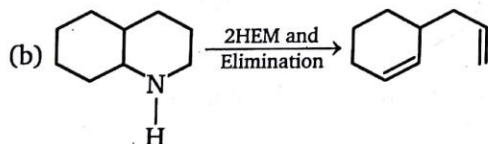
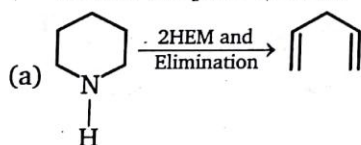
Even no. of HEM

Follow the path of HEM

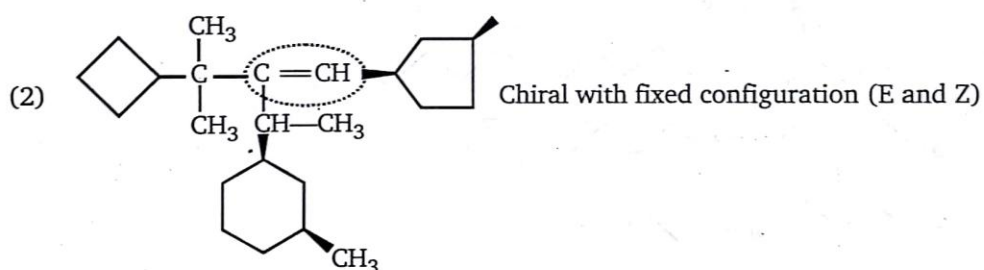
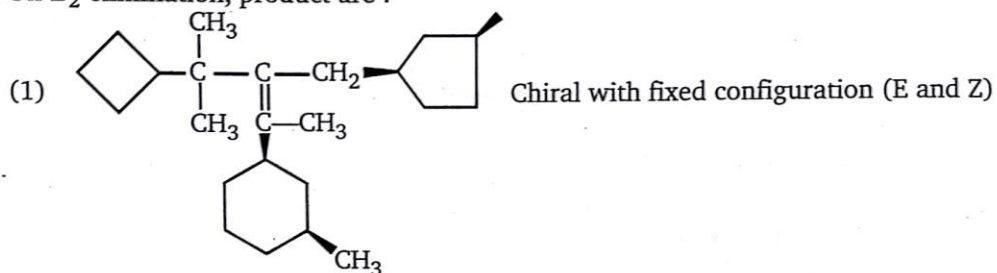
(a) $\xrightarrow{\text{2HEM and Elimination}}$

(b) $\xrightarrow{\text{2HEM and Elimination}}$

(c) $\xrightarrow{\text{3HEM and Elimination}}$

(d $\xrightarrow{\text{1HEM and Elimination}} CH_2=CH_2$

71. (b) On E_2 elimination, product are :

(1) Chiral with fixed configuration (E and Z)

(2) Chiral with fixed configuration (E and Z)

Level-2

1. (A) More good leaving group more E_2 reaction.

(B) (P) Anti-elimination

(Q) C—H weak bond than C—D

(R) Resonance stable alkene

(S) Acidic hydrogen

(C) Consider conformer.

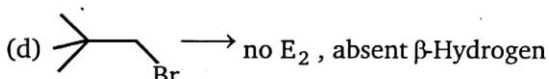
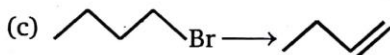
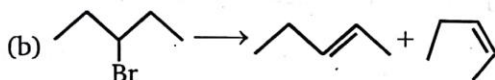
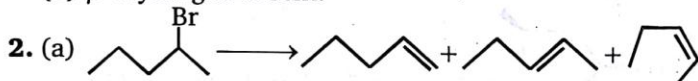
(D) Anti elimination

(E) β–Hydrogen absent.

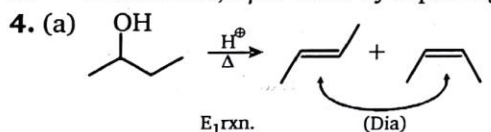
2. (a) Br

(b) Br

(c) Br

(d) Br → no E_2, absent β-Hydrogen

3. Formed $C\alpha$, $C\beta$ π-bond by replacing $C\alpha - N$ σ-bond.

4. (a) OH $\xrightarrow[\Delta]{H^{\oplus}}$ +

E_1rxn. (Dia)

Carbocation due to acidic medium.

(b) Br $\xrightarrow[\Delta]{\text{alc. KOH}}$ +

E_2 rxn. one step rxn.

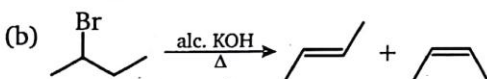
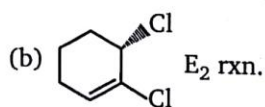
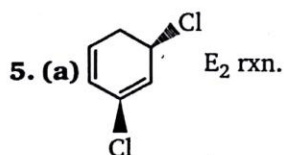
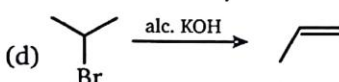
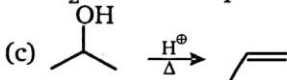
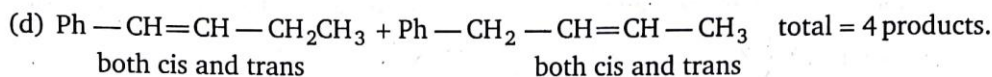
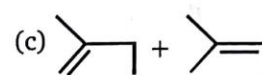
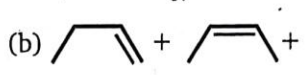
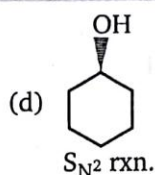
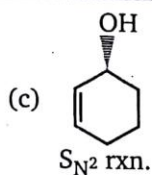
(c) OH $\xrightarrow[\Delta]{H^{\oplus}}$

(d) Br $\xrightarrow{\text{alc. KOH}}$

5. (a) Cl Cl E_2 rxn. (b) Cl Cl E_2 rxn.

(c) OH — S_N2 rxn. (d) OH — S_N2 rxn.

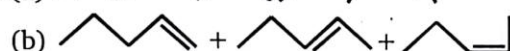
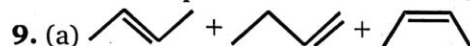
6. (a) (b) + + (c) +

(d) Ph — CH=CH — CH_2CH_3 + Ph — CH_2 — CH=CH — CH_3 total = 4 products.
both cis and trans both cis and trans

7. Consider basic information.

8. Consider cope elimination in which syn elimination take place.

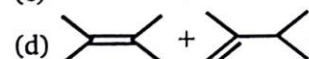
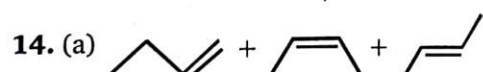
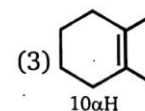
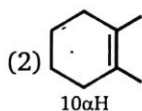
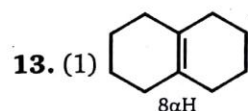
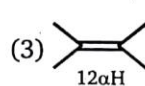
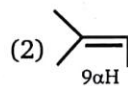
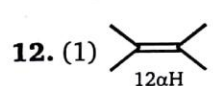
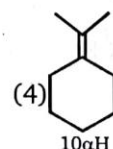
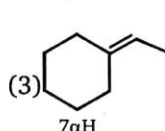
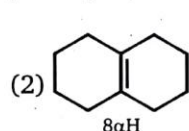
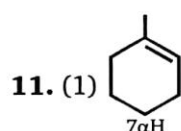
9. (a) + +

(b) + +

(c) +

(d) No β-hydrogen so no E_2 reaction.

10. (1) 2 mole $NaNH_2$ for E_2 and 1 mole for acid-base reaction.

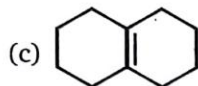
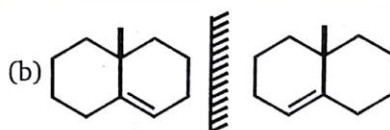
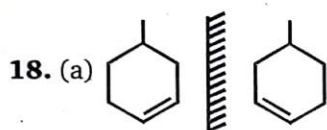
(2) 2 mole $NaNH_2$ for E_2

(3) 2 mole $NaNH_2$ for E_2 and 1 mole for acid-base.

15. Basic information

16. Basic information

17. 3° alkyl halide, do not show S_N2

Solution Advanced Problems in Organic Chemistry Part 2 upto Page 240 Aldol and Cannizaro Reactions by M S Chouhan Vibrant Academy Kota for IIT JEE Main Advanced Chemistry Olympiad

18.

(d) Violation of Bredt rule

19. Number of C — N bond is equal to number of Hoffmann exhaustive elimination.

20. 3(C — N) + (3)(, ,)

21. $CH_3-CH(OEt)-CH(CH_3)-CH_3$ (2) + $CH_3-CH_2-C(CH_3)(OEt)-CH_3$ (1)

$CH_3-CH-CH(CH_3)-CH_3$ (1) $CH_3-CH=C(CH_3)_2$ (1)

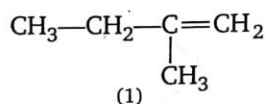
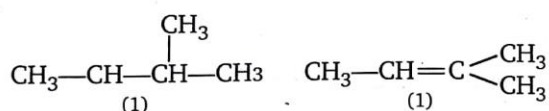
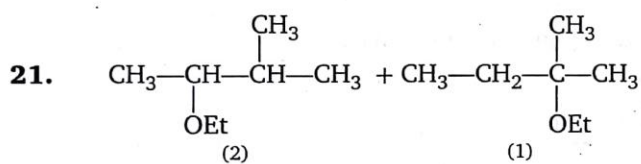
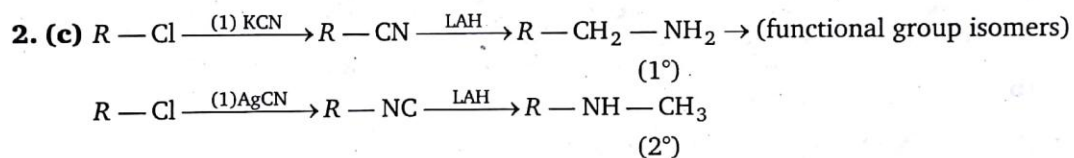
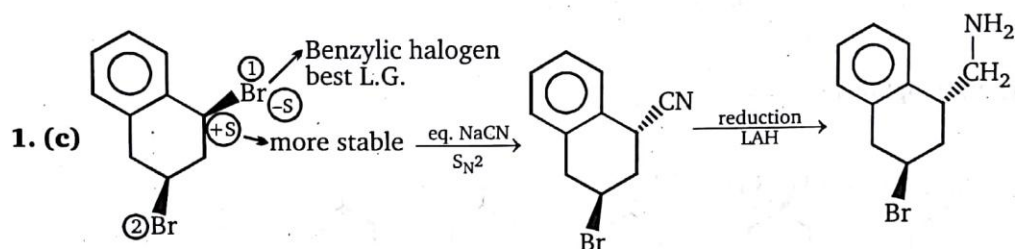
$CH_3-CH_2-C(CH_3)=CH_2$ (1)

5(c) Alkyl Halides

Level-1

1. (c)

2. (c) $R-Cl \xrightarrow{(1)\ KCN} R-CN \xrightarrow{LAH} R-CH_2-NH_2 \rightarrow$ (functional group isomers)
(1°)

$R-Cl \xrightarrow{(1) AgCN} R-NC \xrightarrow{LAH} R-NH-CH_3$
(2°)

3. (b) 'Cl' is best L.G. & inversion of configuration takes place.

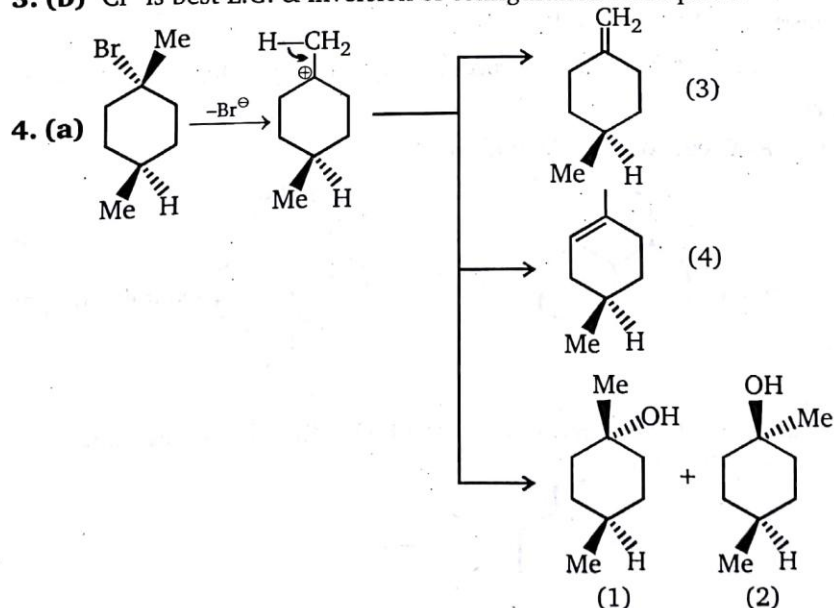
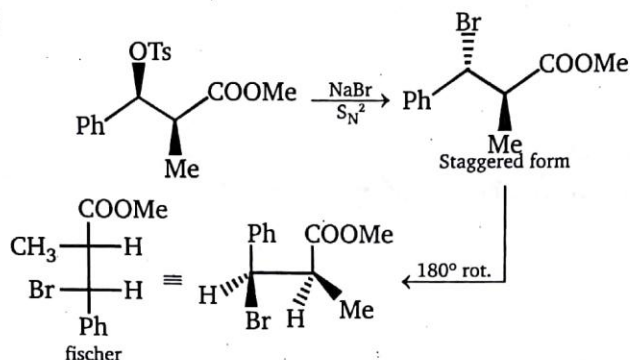
4. (a)

5. (a)

OTs, Ph, COOMe, Me $\xrightarrow[S_N2]{NaBr}$ Br, Ph, COOMe, Me — Staggered form

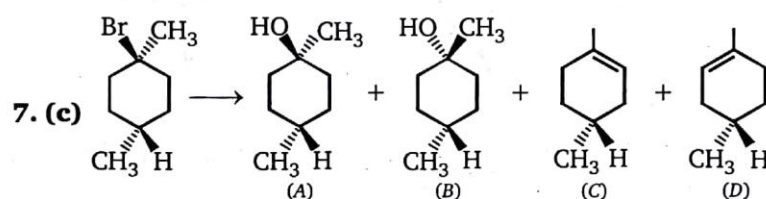
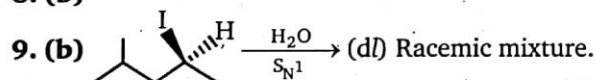
$\downarrow$ 180° rot.

Fischer: COOMe; CH_3—H; Br—H; Ph $\equiv$ Ph, COOMe, H, Br, H, Me

fischer

6. (a) Nucleophilicity $\propto \dfrac{1}{\text{size of Nu}^\ominus}$

7. (c) Br, CH_3 / CH_3, H $\longrightarrow$ HO, CH_3 / CH_3, H (A) + HO, CH_3 / CH_3, H (B) + CH_3, H (C) + CH_3, H (D)

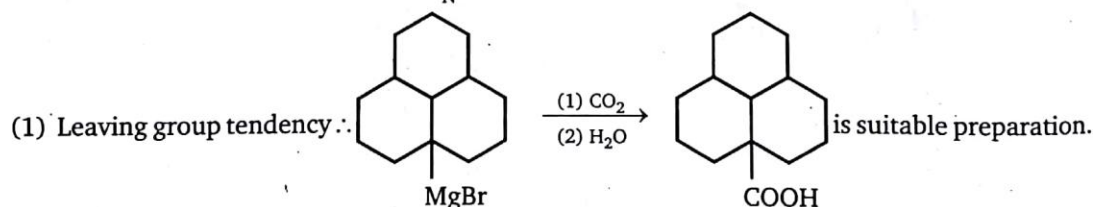
8. (b)

9. (b) I, H $\xrightarrow[S_N1]{H_2O}$ (*dl*) Racemic mixture.

10. (d) Informative question [All are correct]

11. (c) At bridge head S_{N^2} doesn't take place. According to bredt's rule bridge head carbon can't be sp^2-hybridized.

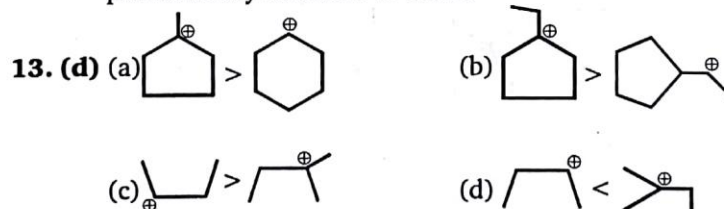
(NaI+ Acetone)+*R*–*X* reaction S_{N^2} depends on

(1) Leaving group tendency ∴

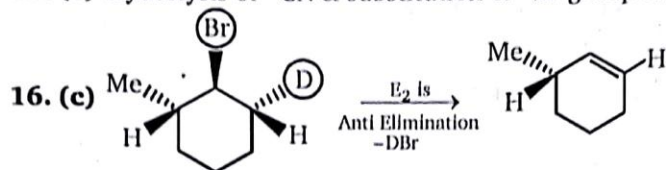
is suitable preparation.

(2) Steric crowding.

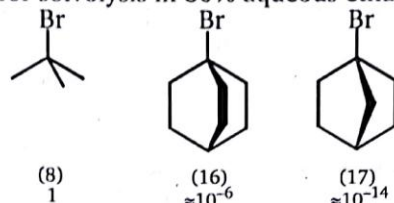
12. (c) $EtS^\ominus$ is weak base than $EtO^\ominus$ but more $Nu^\ominus$ than $EtO^\ominus$ due to less solvation and more polarizability of donar 'S' atom.

13. (d) (a) ⊕ > ⊕ (b) ⊕ > ⊕

(c) ⊕ > ⊕ (d) ⊕ < ⊕

14. (a) S_{N^1} reaction.

15. (c) Hydrolysis of –CN & substitution of –Br group takes place in given reaction.

16. (c) Me, H, (Br), (D), H $\xrightarrow[\text{Anti Elimination, } -DBr]{E_2 \text{ is}}$ Me, H, H

17. (c) The effect of structure on relative reactivity may be seen particularly clearly when a halogen atom is located at the bridgehead of a bicyclic system. Thus the following rates were observed for solvolysis in 80% aqueous ethanol at 25°:

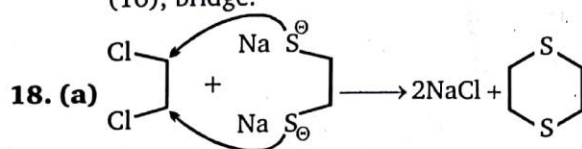
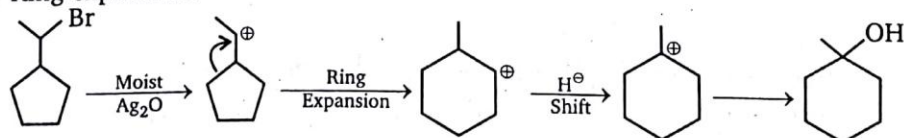
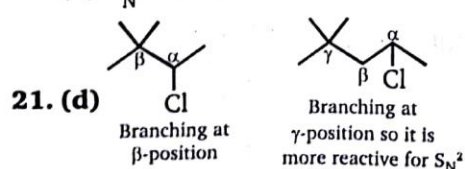
Br (8) 1 — Br (16) $\approx 10^{-6}$ — Br (17) $\approx 10^{-14}$

All are tertiary halides so that attack by the S_{N^2} mode would not be expected to occur on (16) or (17) any more than it did on (8). S_{N^2} attack 'from the back' on the carbon atom carrying Br would in any case be prevented in (16) and (17) both sterically by their cagelike structure, and also by the impossibility of forcing their fairly rigid framework through transition states with the required planar distribution of bonds to the bridgehead carbon atom. Solvolysis via rate- limiting formation of the ion pair (S_{N^1}), as happens with (8) is also inhibited because the resultant carbocations from (16) and (17) would be unable, because of their rigid frameworks, to stabilise themselves by collapsing to the stable planar state. These carbocation intermediates are thus of very much higher energy level than usual, and therefore are formed only slowly and with reluctance. The very greatly reduced solvolysis rate of (17) compared with (16) reflects the greater rigidity about the bridgehead (cationic) carbon with a one carbon (17), than with a two- carbon (16), bridge.

18. (a) Cl, Cl + Na $S^{\ominus}$, Na $S^{\ominus}$ ⟶ 2NaCl + S, S

19. (c) Ring expansion.

Br $\xrightarrow[Ag_2O]{\text{Moist}}$ ⊕ $\xrightarrow{\text{Ring Expansion}}$ ⊕ $\xrightarrow[\text{Shift}]{H^{\ominus}}$ ⊕ ⟶ OH

20. (b) S_{N^2} reaction.

21. (d) β, α, Cl — Branching at β-position; γ, β, α, Cl — Branching at γ-position so it is more reactive for S_{N^2}

22. (d) All products synthesized by $S_{N}2$

(1) Cyclohexyl$-CH_2-Cl \xrightarrow[DMSO]{NaOH}$ Cyclohexyl$-CH_2-OH$

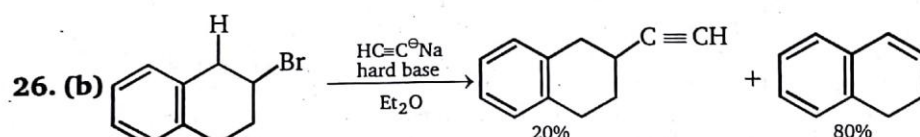
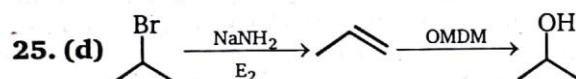
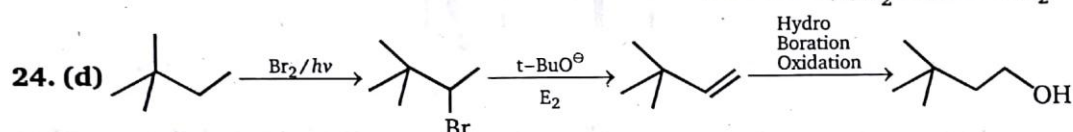
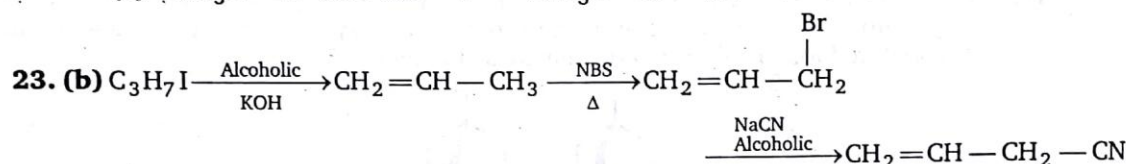
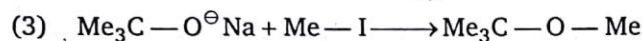
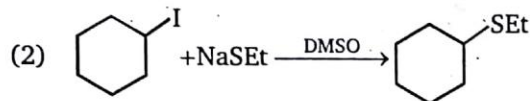
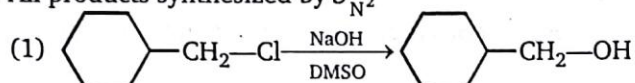
(2) Cyclohexyl iodide $+ NaSEt \xrightarrow{DMSO}$ Cyclohexyl$-SEt$

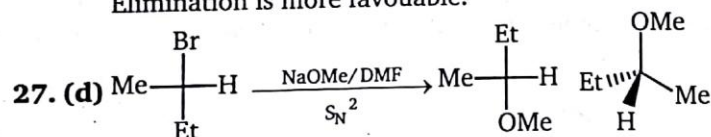
(3) $Me_3C-O^{\ominus}Na + Me-I \longrightarrow Me_3C-O-Me$

23. (b) $C_3H_7I \xrightarrow[KOH]{Alcoholic} CH_2=CH-CH_3 \xrightarrow[\Delta]{NBS} CH_2=CH-CH_2Br \xrightarrow[Alcoholic]{NaCN} CH_2=CH-CH_2-CN$

24. (d) $\xrightarrow{Br_2/hv}$ (Br) $\xrightarrow[E_2]{t\text{-}BuO^{\ominus}}$ $\xrightarrow{\text{Hydro Boration Oxidation}}$ OH

25. (d) Br $\xrightarrow[E_2]{NaNH_2}$ $\xrightarrow{OMDM}$ OH

26. (b) H, Br $\xrightarrow[Et_2O]{HC\equiv C^{\ominus}Na \text{ hard base}}$ $C\equiv CH$ (20%) + (80%)

Elimination is more favouable.

27. (d) $Me-C(Br)(Et)-H \xrightarrow[S_N2]{NaOMe/DMF} Me-C(Et)(OMe)-H$ Et, OMe, Me, H

28. (a) Informative question.

29. (a) Rate of reaction of alcohol with H—Br $\propto$ Stability of $C^{\oplus}$ formed in R.D.S.

30. (d)

$Me_2CH=CH-Me + Me_2CH_2-CH=CH_2$

$CH_3-CH(CH_3)-CH(CH_3)-OTs \xrightarrow[75°C, -OTs]{AcOH} CH_3-CH(CH_3)-\overset{\oplus}{C}H(CH_3) \longrightarrow CH_3-\overset{\oplus}{C}(CH_3)-CH_2CH_3$

$\downarrow AcOH$: $Me_2CH-CH(OAc)-Me$ (dl) (d & l)

$\downarrow AcOH$: $Me-C(OAc)(Me)-CH_2CH_3$

31. (b) $Ph-CCl_3 \xrightarrow[\text{Milk of lime}]{Ca(OH)_2} Ph-C(OH)_2(OH) \xrightarrow{-H_2O} Ph-COOH$

32. (b) $Br-CH_2-CH_2-CH_2-CH_2-Br + Me-\ddot{N}H_2 \xrightarrow{-Br^\ominus} \overset{\ominus}{Br} + Me-N(H)-CH_2-CH_2-CH_2-CH_2-Br \xrightarrow{-H} Br-CH_2-CH_2-CH_2-CH_2-\ddot{N}H-Me \xrightarrow{-Br^\ominus}$ (cyclic $\overset{\oplus}{N}$–H, Me) $\xrightarrow[-HBr]{Br^\ominus}$ N-Me pyrrolidine

33. (d) (ⓒ D, ⓐ Br, ⓑ COOMe, ⓓ H) 'S' configuration $\xrightarrow[EtOH]{KCN}$ (ⓑ NC, ⓒ D, ⓐ COOMe, H) 'S' configuration

less polar S_N2

34. (d) Cl–CH₂CH₂CH₂CH(Cl)CH₃ $\xrightarrow[(1\ mole)]{NaI}$ I–CH₂CH₂CH₂CH(Cl)CH₃

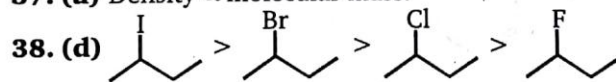
rate of S_{N^2} faster at 1° than 2°

35. (c) $C_2H_5OH + NaCl \not\longrightarrow C_2H_5Cl + NaOH$

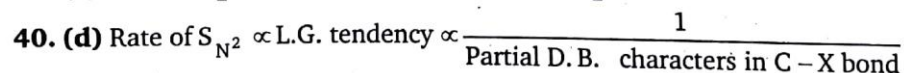
$Cl^\ominus$ can not replace OH group because 'Cl' is best L.G.

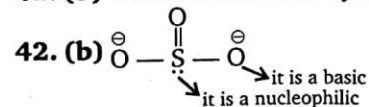
36. (c) propanol (–OH) $\xrightarrow[\text{pyridine} \mid S_{N^2}]{SOCl_2}$ propyl chloride (–Cl)

37. (a) Density ∝ molecular mass.

38. (d) 2-iodobutane > 2-bromobutane > 2-chlorobutane > 2-fluorobutane

Decreasing order of rate of S_{N^2} reaction.

39. (c) $Ph-CH_2-Cl + KCN \xrightarrow{EtOH} Ph-CH_2-CN$

40. (d) Rate of $S_{N^2} \propto$ L.G. tendency $\propto \dfrac{1}{\text{Partial D.B. characters in C} - \text{X bond}}$

41. (b) Williamson's ether synthesis is S_{N^2} not possible in 3° alkyl halide.

42. (b) $\overset{\ominus}{O}-\underset{..}{S}(=O)-\overset{\ominus}{O}$ → it is a basic (O); → it is a nucleophilic (S)

(Sulphur is better nucleophile than oxygen.) (But oxygen is better base than sulphur)

(*A*) is formed by acid-base reaction therefore oxygen will react.
(*B*) is formed by electrophile and nucleophile reaction therefore sulphur will react.

Level-2

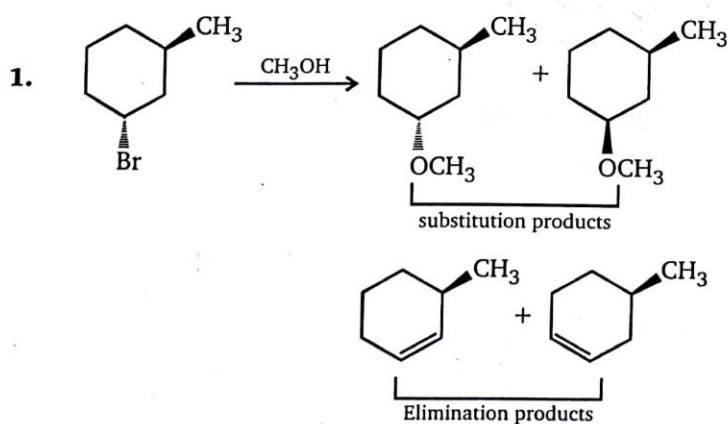
1. Vinyl and aryl halide do not show substitution and elimination.
2. (a) 1° resonance stabilized transition state will be more reactive.
(b) 1° resonance stabilized transition state will be more reactive.
(c) Good leaving group.
3. Basic information of organic reaction.

SUBJECTIVE PROBLEMS

1. CH$_3$, Br (cyclohexane) $\xrightarrow{CH_3OH}$ CH$_3$, OCH$_3$ + CH$_3$, OCH$_3$

substitution products

CH$_3$ + CH$_3$

Elimination products

6 Alcohol, Ethers And Epoxides

Level-1

1. (c) $\xrightarrow{H_2SO_4}$

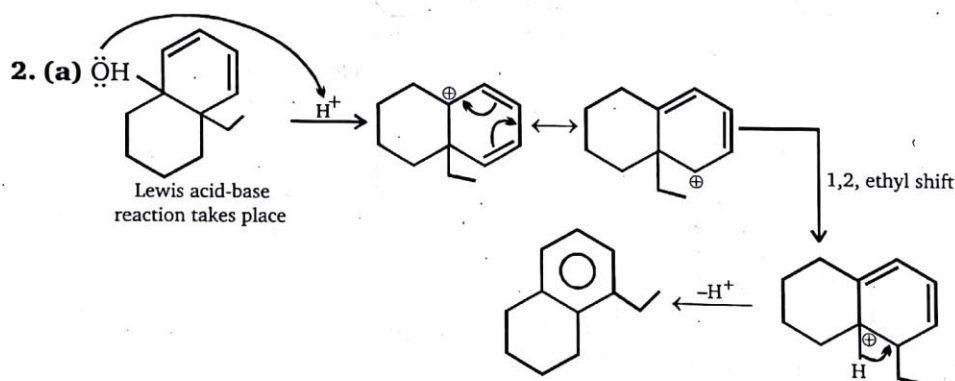
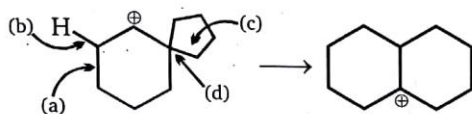
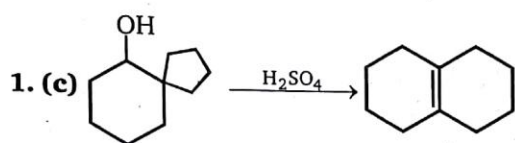
(b) H, (c), (a), (d) →

2. (a) ÖH $\xrightarrow{H^+}$ ⟷

Lewis acid-base reaction takes place

1,2, ethyl shift

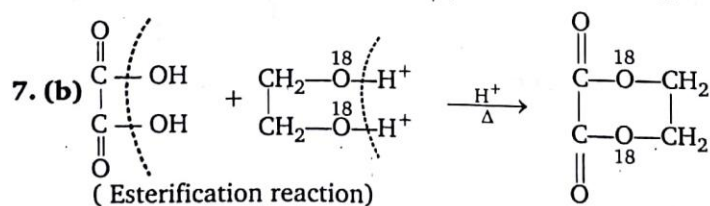
$\xleftarrow{-H^+}$

H

3. (b) More nucleophilic nitrogen will attack.

4. (c) $LiAlH_4$ will reduce aldehyde, ketone and ester.

5. (b) $NaBH_4$ will not reduce ester.

6. (b) In esterification acid gives $OH^{\ominus}$ whereas alcohol gives H^+.

Product of the reaction is methyl benzoate $Ph-\overset{\overset{O}{||}}{C}-\overset{18}{O}-CH_3$

7. (b) (COOH)₂ + $HO^{18}CH_2CH_2{}^{18}OH \xrightarrow[\Delta]{H^+}$ cyclic diester with ^{18}O in ring

(Esterification reaction)

8. (a) $CH_3-CH(OH)-CH_3 \xrightarrow{[O]} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

2° alcohol more easily oxidised than 3° alcohol.

9. (b) 2-hydroxycyclopentanecarboxylic acid $\xrightarrow{K_2Cr_2O_7}$ 2-oxocyclopentanecarboxylic acid (β-ketoacid) $\xrightarrow{\Delta}$ cyclopentanone $+ CO_2$

Decarboxylation takes place.

10. (b) 3° alcohol when reacts with HBr it gives S_{N^1} reaction.

1-methylcyclohexanol $\xrightarrow[(S_{N^1})]{H-Br}$ 1-methylcyclohexyl cation (3°carbocation)

most stable carbocation.

11. (b) $CH_3-\overset{O}{\overset{\|}{C}}-C_6H_{10}-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{LiAlH_4} CH_3-\overset{OH}{\overset{|}{CH}}-C_6H_{10}-CH_2OH$

$-COOH \longrightarrow -CH_2OH$
1° alcohol

$-\overset{O}{\overset{\|}{C}}- \longrightarrow -\overset{OH}{\overset{|}{CH}}-$
2° alcohol

12. (b) $HO_2C-C_6H_4-CO_2H \xrightarrow[H_2SO_4,\Delta]{2CH_3OH} CH_3O-\overset{O}{\overset{\|}{C}}-C_6H_4-\overset{O}{\overset{\|}{C}}-OCH_3$

esterification

13. (a) 1-cyclopentyl diol $(C(OH)Ph_2)$ $\xrightarrow[\Delta]{H^+}$ cyclopentanol with $\overset{\oplus}{C}Ph_2$ $\xrightarrow{\text{Ring expansion}}$ cyclohexyl cation bearing $\ddot{O}-H$ and CPh_2 $\xrightarrow{-H^{\oplus}}$ 2,2-diphenylcyclohexanone

Most stable (3°) carbocation

14. (a) OH, OH, OMe $\xrightarrow{H^+}$ $CH_3O-C_6H_4-\overset{O}{\overset{\|}{C}}-\overset{CH_3\ CH_3}{C}-\underset{OH}{CH}-Ph$ $\xrightarrow{H^{\oplus}}$ $CH_3O-C_6H_4-\overset{O}{\overset{\|}{C}}-C-\overset{\oplus}{C}H-Ph$ $\xrightarrow[\text{substitution}]{\text{Electrophilic aromatic}}$ –OMe

Positive charge on 3-membered ring is unstable therefore σ –bond of cyclopropane will attack on $H^{\oplus}$.

15. (a) OH, O $\xrightarrow{H^+}$:OH, ⊕, O (stable) **(Reso stabilized)** ⟶ O, O

16. (a) O, O (reduced – COOH) $\xrightarrow{H^+}$ H, ⊕O, O ⟶ H–$\overset{\oplus}{O}$, O ⟶ O, O

17. (d) $LiAlH_4$ reduces esters into alcohol.

18. (a) OH, OH (Resorcinol) ⇌ O, O (active methylene group) (keto form) $\xrightarrow{I_2+NaOH}$ O, $\overset{\ominus}{O}\overset{\oplus}{Na}$, CH_2, CO_2Na $+CHI_3$

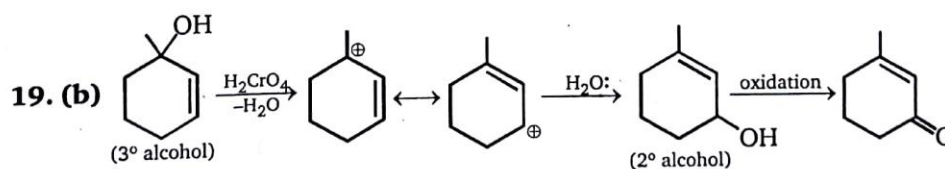
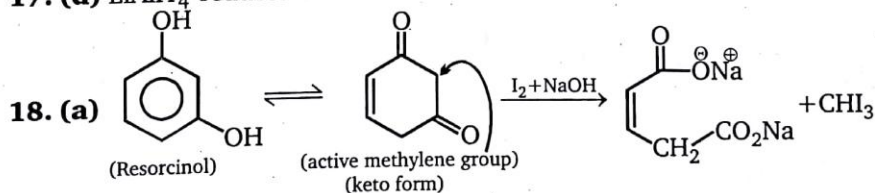
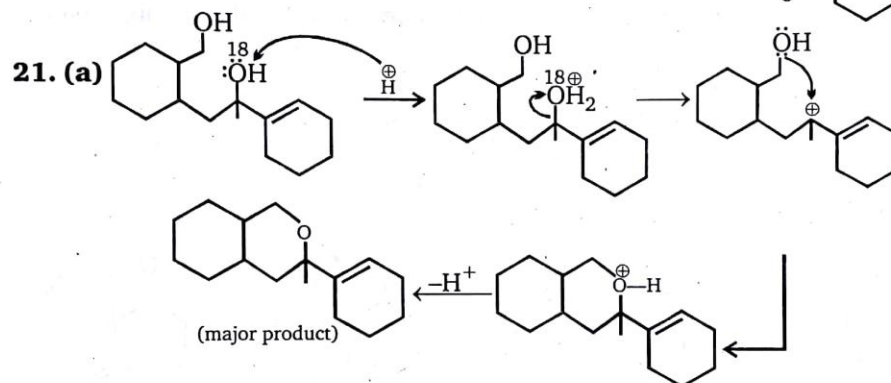
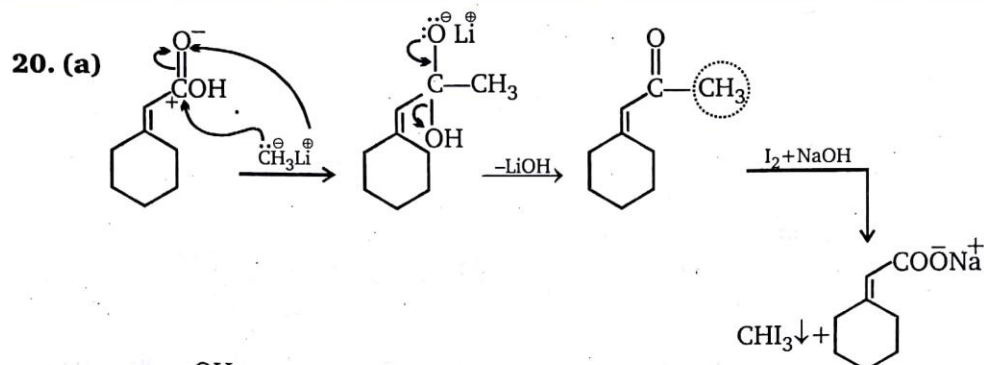
19. (b) OH (3° alcohol) $\xrightarrow[-H_2O]{H_2CrO_4}$ ⊕ ⟷ ⊕ $\xrightarrow{H_2O:}$ OH (2° alcohol) $\xrightarrow{\text{oxidation}}$ O

No oxidation

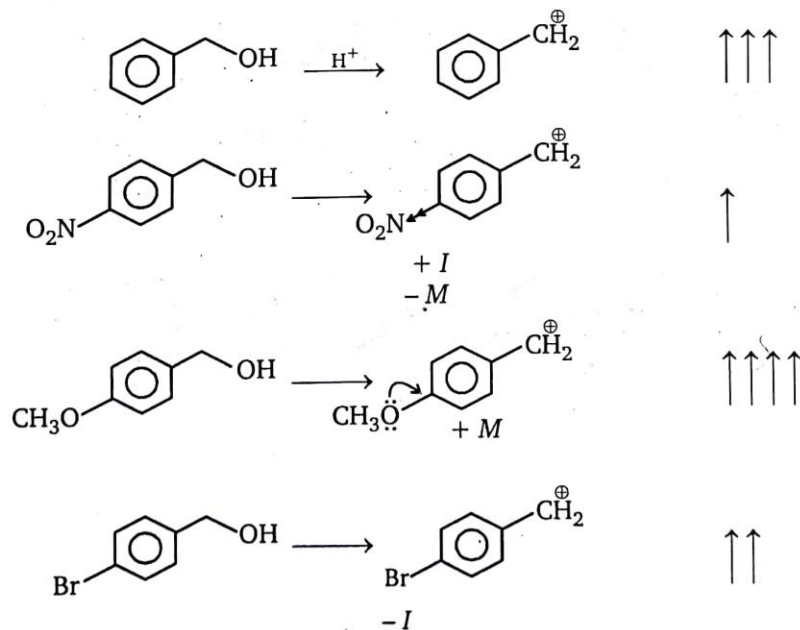
20. (a)

CH_3Li ; $-LiOH$; $I_2 + NaOH$; $CHI_3\downarrow + $; COO^-Na^+

21. (a)

(major product)

22. (a) More stable carbocation more is the rate toward HBr (acid).

Stability order of carbocation

OH $\xrightarrow{H^+}$ $\overset{\oplus}{CH_2}$		↑↑↑
O_2N — OH ⟶ O_2N — $\overset{\oplus}{CH_2}$	$+I$, $-M$	↑
CH_3O — OH ⟶ $CH_3\ddot{O}$ — $\overset{\oplus}{CH_2}$	$+M$	↑↑↑↑
Br — OH ⟶ Br — $\overset{\oplus}{CH_2}$	$-I$	↑↑

Rate of reaction ∝ stability of carbocation

23. (d) $P=$ HO OH OH

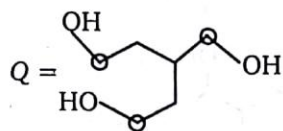
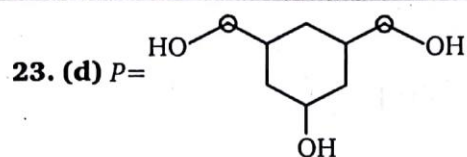
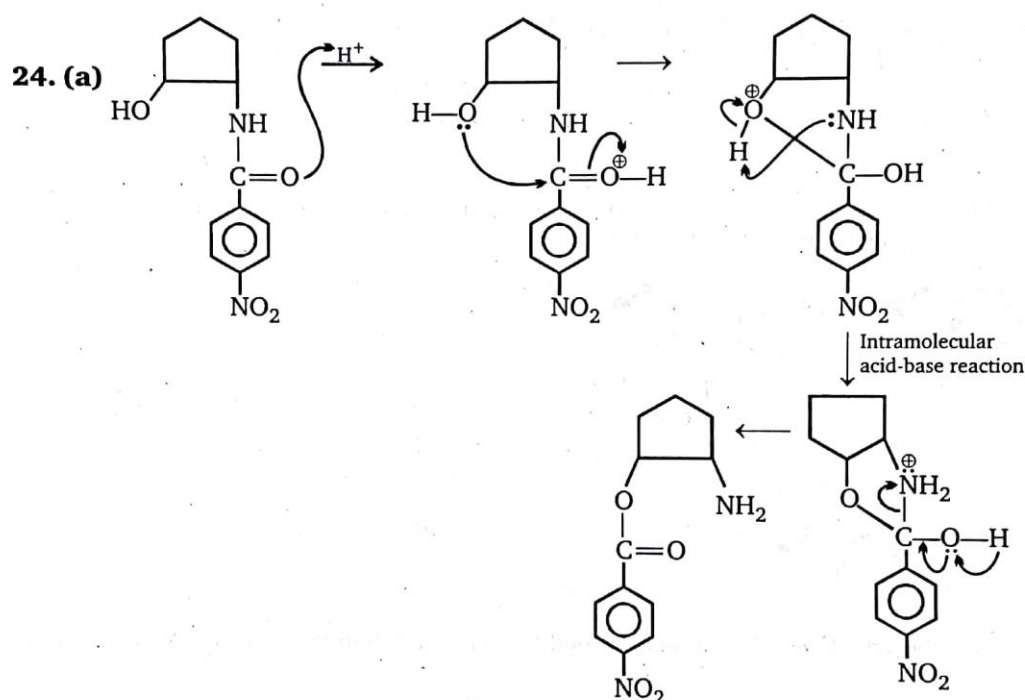
$Q =$ OH OH HO

$P = 2, Q = 3$

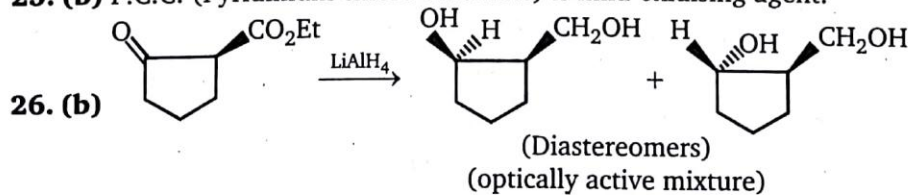
$2 + 3 = \mathbf{5}$

24. (a) HO NH C=O NO_2 $\xrightarrow{H^+}$ H—O NH C=$\overset{\oplus}{O}$—H NO_2 ⟶ $\overset{\oplus}{O}$ H :NH C—OH NO_2

Intramolecular acid-base reaction

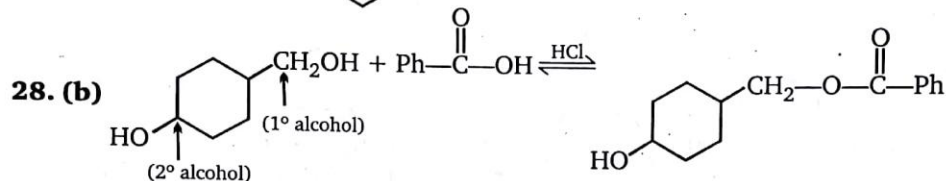
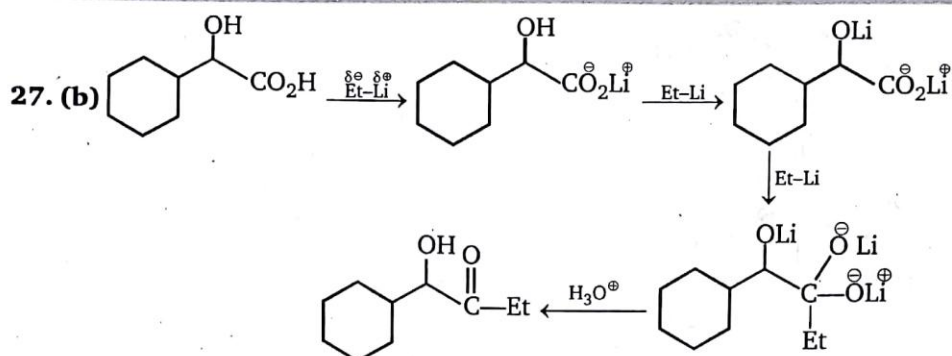
O $\overset{\oplus}{N}H_2$ C—O—H NO_2 ⟶ O NH_2 C=O NO_2

25. (b) P.C.C. (Pyridinium chloro chromate) is mild-oxidising agent.

26. (b) O CO_2Et $\xrightarrow{LiAlH_4}$ OH H CH_2OH + H OH CH_2OH

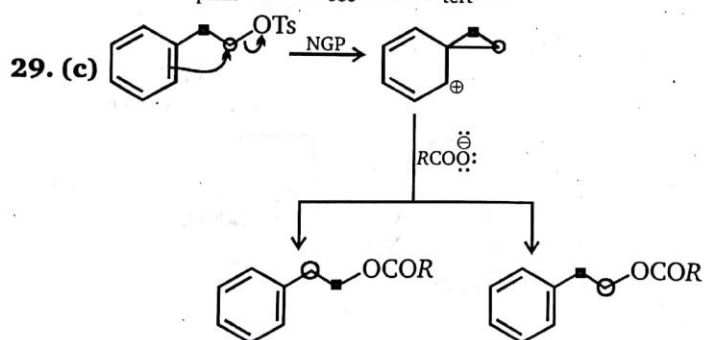
(Diastereomers)
(optically active mixture)

Mechanism of reaction is nucleophilic addition.

27. (b) OH, CO_2H $\xrightarrow{\overset{\delta\ominus}{Et}-\overset{\delta\oplus}{Li}}$ OH, $CO_2^{\ominus}Li^{\oplus}$ $\xrightarrow{Et-Li}$ OLi, $CO_2^{\ominus}Li^{\oplus}$ $\xrightarrow{Et-Li}$ OLi, $O^{\ominus}Li$, C—$O^{\ominus}Li^{\oplus}$, Et $\xrightarrow{H_3O^{\oplus}}$ OH O, C—Et

28. (b) CH_2OH + Ph—C(=O)—OH $\overset{HCl}{\rightleftharpoons}$ CH_2—O—C(=O)—Ph, HO

HO (2° alcohol) (1° alcohol)

Order of nucleophilicity in esterification is (Explained by steric hindrance)

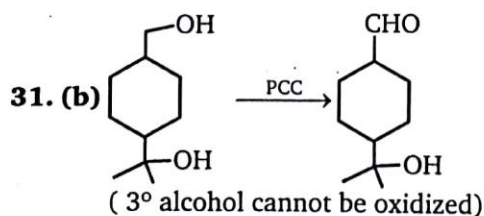
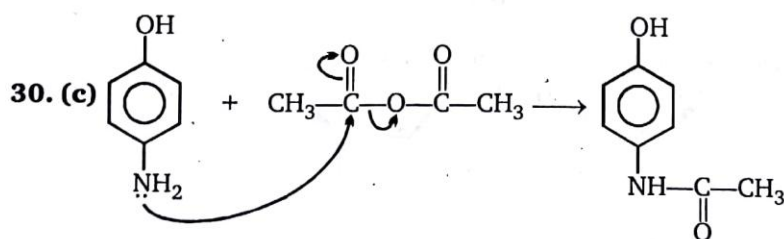
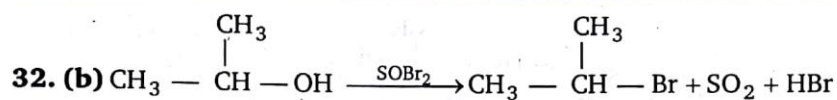
$R_{prim}OH > R_{sec}OH > R_{tert}OH$

29. (c) OTs $\xrightarrow{NGP}$ ⊕ $\xrightarrow{RCO\ddot{O}:^{\ominus}}$ OCOR, OCOR

Both product (*A*) & (*B*) can be obtained by NGP (Neighbouring group participation).

30. (c) OH, NH_2 + CH_3—C(=O)—O—C(=O)—CH_3 ⟶ OH, NH—C(=O)—CH_3

31. (b) —OH, —OH $\xrightarrow{PCC}$ CHO, —OH

(3° alcohol cannot be oxidized)

32. (b) $CH_3-\underset{|}{\overset{CH_3}{CH}}-OH \xrightarrow{SOBr_2} CH_3-\overset{CH_3}{\underset{|}{CH}}-Br + SO_2 + HBr$

Side products are gases.

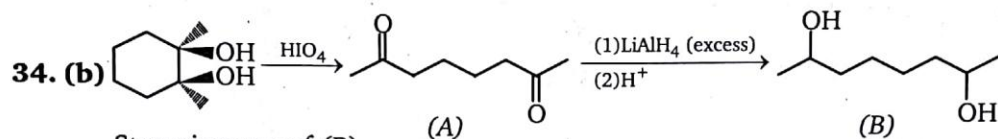
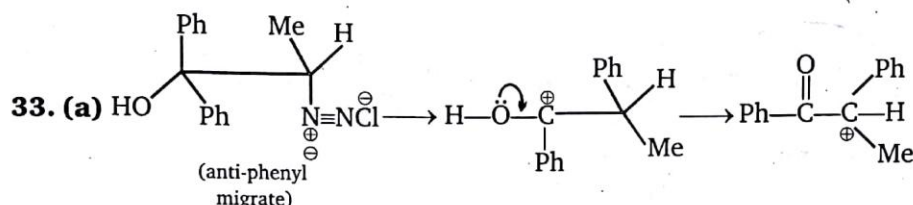
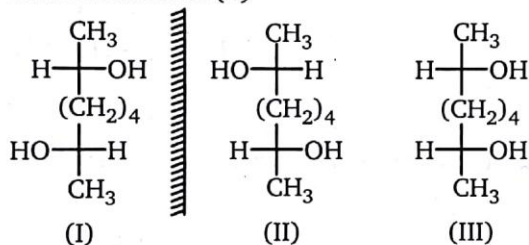
In case of HBr elimination also favours to produce alkene.

33. (a) HO–C(Ph)(Ph)–C(Me)(H)–$\overset{\oplus}{N}\equiv N\overset{\ominus}{Cl}$ ⟶ $H-\ddot{O}-\overset{\oplus}{C}(Ph)-C(Ph)(H)(Me)$ ⟶ $Ph-\overset{O}{\overset{||}{C}}-\overset{\oplus}{C}(Ph)(H)(Me)$

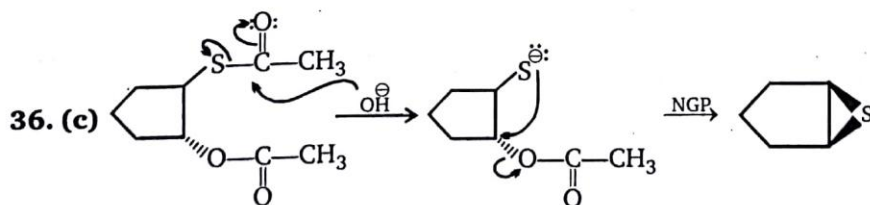
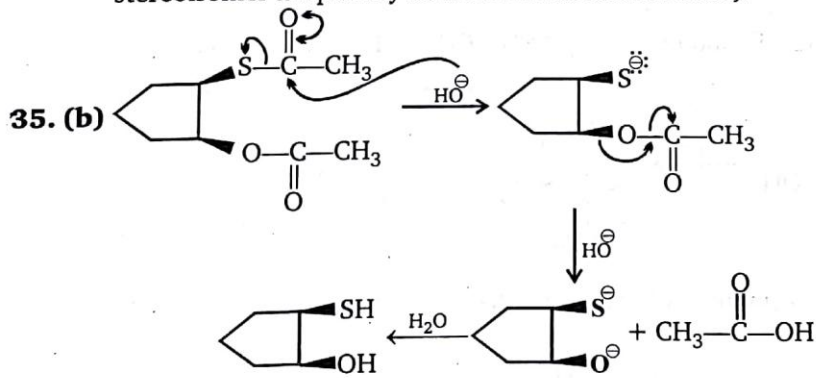
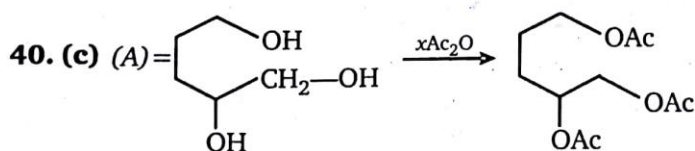
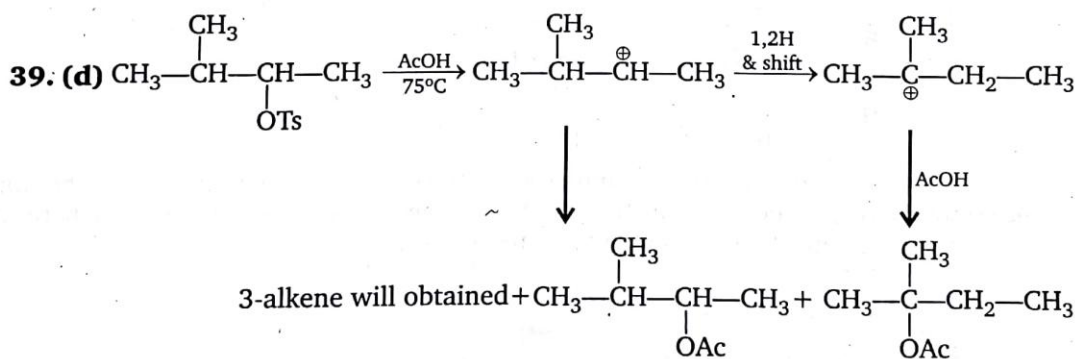
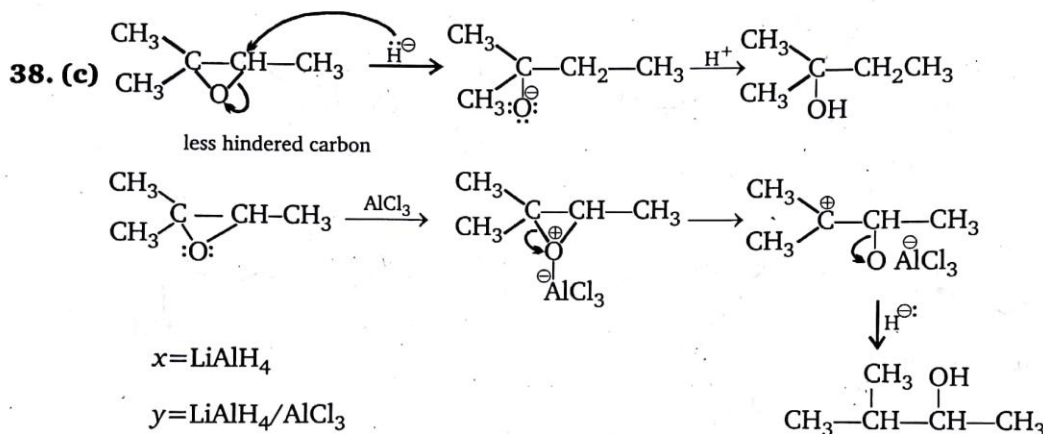
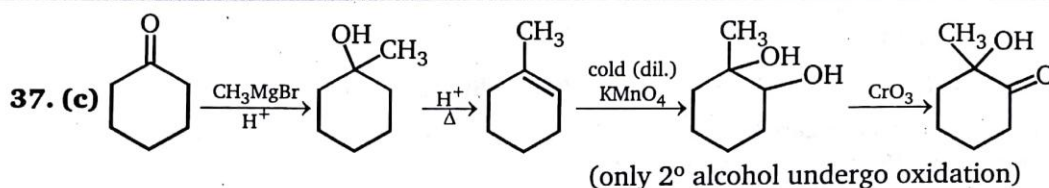
(anti-phenyl migrate)

34. (b) cyclohexane-1,2-diol (OH, OH) $\xrightarrow{HIO_4}$ (A) $\xrightarrow[(2)H^+]{(1)LiAlH_4\text{ (excess)}}$ (B) (OH, OH)

Stereoisomers of (B)

(I)	(II)	(III)
CH_3; H–C–OH; $(CH_2)_4$; HO–C–H; CH_3	CH_3; HO–C–H; $(CH_2)_4$; H–C–OH; CH_3	CH_3; H–C–OH; $(CH_2)_4$; H–C–OH; CH_3

2 chiral centres and plane of symmetry is present in compound (B) so the total stereoisomer of product (B) will be 3 (2 stereoisomers are optically active whereas 1 stereoisomer is optically inactive which is meso form).

35. (b) cyclopentane with $S-\overset{O}{\overset{||}{C}}-CH_3$ and $O-\underset{O}{\underset{||}{C}}-CH_3$ $\xrightarrow{HO^{\ominus}}$ cyclopentane with $S^{\ominus}$ and $O-\underset{O}{\underset{||}{C}}-CH_3$ $\xrightarrow{HO^{\ominus}}$ cyclopentane with $S^{\ominus}$ and $O^{\ominus}$ + $CH_3-\overset{O}{\overset{||}{C}}-OH$ $\xrightarrow{H_2O}$ cyclopentane with SH and OH

36. (c) cyclopentane with $S-\overset{O}{\overset{||}{C}}-CH_3$ and $O-\underset{O}{\underset{||}{C}}-CH_3$ $\xrightarrow{OH^{\ominus}}$ cyclopentane with $S^{\ominus}$ and $O-\underset{O}{\underset{||}{C}}-CH_3$ $\xrightarrow{NGP}$ bicyclic episulfide (S)

Number of alcohol is number of moles of anhydride consumed.

$\therefore$ 3

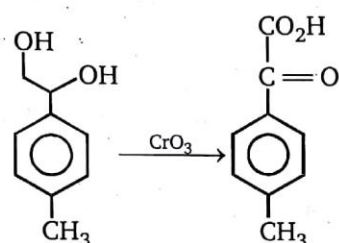
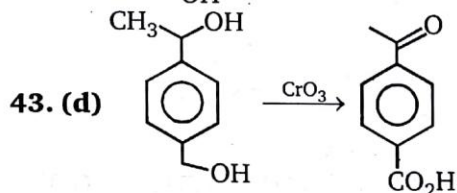
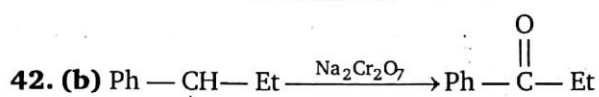
41. (b) (R) & (S)-2-butanol + (R,R–) tartaric acid

↓

(Diastereomer) [RR+RS]

42. (b) Ph — CH(OH) — Et $\xrightarrow{Na_2Cr_2O_7}$ Ph — C(=O) — Et

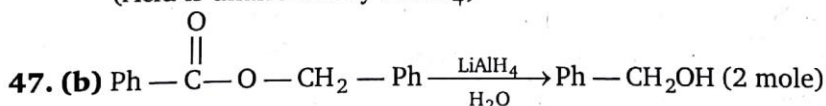
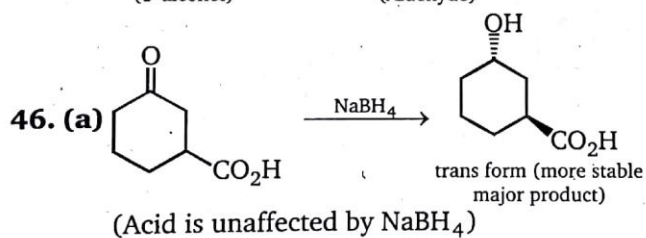
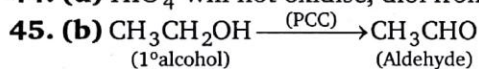
43. (d) CH_3, OH ... OH $\xrightarrow{CrO_3}$ O ... CO_2H

OH, OH ... CH_3 $\xrightarrow{CrO_3}$ CO_2H, C=O ... CH_3

44. (d) HIO_4 will not oxidise, diol from 1, 3 atom & not used for cleavage of ether.

45. (b) CH_3CH_2OH (1°alcohol) $\xrightarrow{(PCC)}$ CH_3CHO (Aldehyde)

46. (a) O ... CO_2H $\xrightarrow{NaBH_4}$ OH ... CO_2H trans form (more stable major product)

(Acid is unaffected by $NaBH_4$)

47. (b) Ph — C(=O) — O — CH_2 — Ph $\xrightarrow[H_2O]{LiAlH_4}$ Ph — CH_2OH (2 mole)

48. (b) $Cr^{+6} \longrightarrow Cr^{+3}$ (PCC oxidises 1° alcohol to aldehyde)

49. (a) cis-2-butene when undergo syn-addition meso compound will form.

50. (b) Et — C(=O) — CH_3 + CH_3CH_2MgI $\xrightarrow[(2)H^{\oplus}]{}$ Et—C(OH)(Et)—CH_3

3°alcohol (cannot be oxidized)

51. (a) C_6H_5—C(=O)CH_3 $\xrightarrow[CH_3OH]{NaBD_4}$ C_6H_5—C(OH)(D)CH_3

(Nucleophilic addition takes place)

52. (c) $CH_3-CH_2-CH_2-OH \xrightarrow{PCC} CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H + CH_3-\overset{\ominus}{C}H(CH_3)-\overset{\oplus}{Li}$

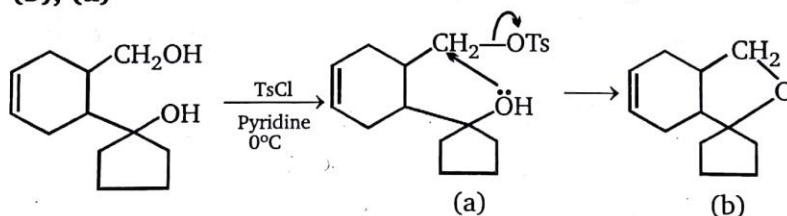
$\xrightarrow{H_3O^{\oplus}} CH_3-CH_2-CH(OH)-CH(CH_3)_2 \xrightarrow{Na_2Cr_2O_7}$ (2-methylpentan-3-one)

53. (c) (II) HO–CH₂–CH(CH₃)–CH₂–OH $\xrightarrow[aq.\ H_2SO_4]{CrO_3}$ $HO_2C-CH(CH_3)-CO_2H$ (Gem) $\xrightarrow[(-CO_2)]{\Delta} CH_3-CH_2-CO_2H$

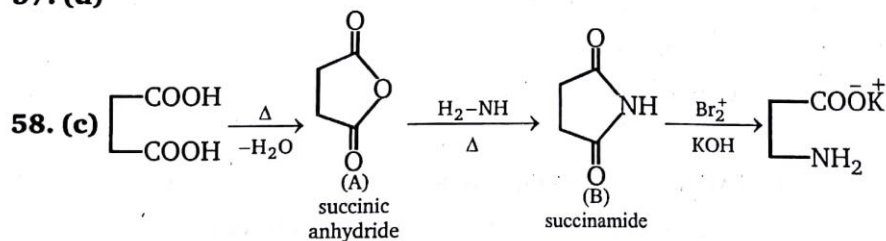
(IV) $CH_3-CH(OH)-CH_2-CH_2-OH \xrightarrow[dil.\ H_2SO_4]{CrO_3} CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OH$ (β-keto acid) $\xrightarrow{\Delta} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CO_2$

54. (c) HIO_4 cannot oxidise, ether and carboxylic acid.

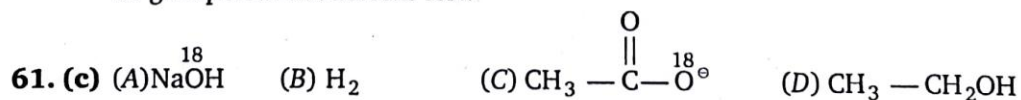
55-56. (b), (a)

(cyclohexene with CH_2OH and spiro-cyclopentyl OH) $\xrightarrow[0°C]{TsCl,\ Pyridine}$ (a) (CH_2-OTs, $\ddot{O}H$) $\longrightarrow$ (b) (cyclic ether, CH_2–O)

1° alcohol better nucleophile than 2° alcohol.

57. (d)

58. (c) $\begin{matrix}CH_2-COOH\\CH_2-COOH\end{matrix} \xrightarrow[-H_2O]{\Delta}$ (A) succinic anhydride $\xrightarrow[\Delta]{H_2-NH}$ (B) succinamide $\xrightarrow[KOH]{Br_2^+}$ $\begin{matrix}CH_2-CO\bar{O}\overset{+}{K}\\CH_2-NH_2\end{matrix}$

59. (A)d (B) b (C) a

60. (c) CH_3-CH_2OH, CH_3CHO, $CH_3-CH(OH)-CH_3$

all give positive iodoform test.

61. (c) (*A*) $Na^{18}OH$ (*B*) H_2 (*C*) $CH_3-\overset{O}{\overset{\|}{C}}-{}^{18}O^{\ominus}$ (*D*) CH_3-CH_2OH

62. A – b ; B – b

(A) $\xrightarrow{NaOH}$ $CO_2^{\ominus}$ / NO_2 (B) + OH, CH_3, O (C)

63. (b) OH (1° alcohol)

Br_2 → Br, Br

Na → $\bar{O}\overset{+}{Na}$ + 1/2 $H_2\uparrow$

H_2CrO_4 → COOH

L.R. → No reaction because reactant is 1° alcohol

64. (c) (L) $C_6H_{11}-\overset{O}{\overset{||}{C}}-\overset{\ominus}{O}\overset{\oplus}{Li}$ (M) $C_6H_{11}-\overset{O}{\overset{||}{C}}-O-CH_3$

(N) $C_6H_{11}-\overset{O}{\overset{||}{C}}-O-H$

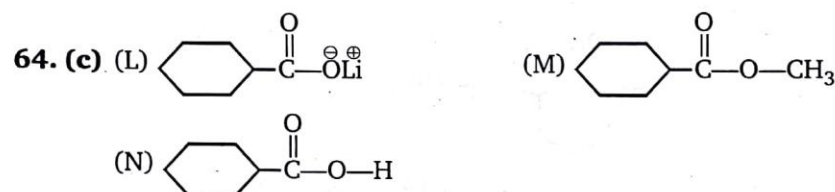
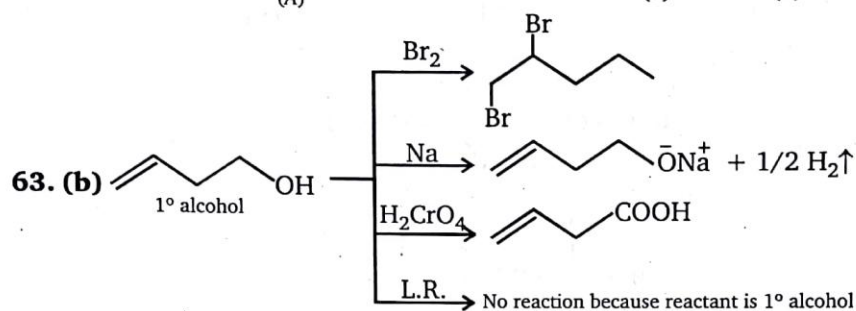
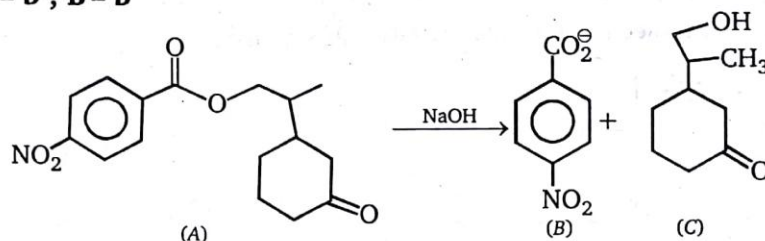
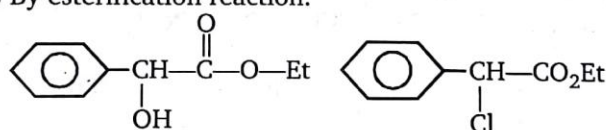
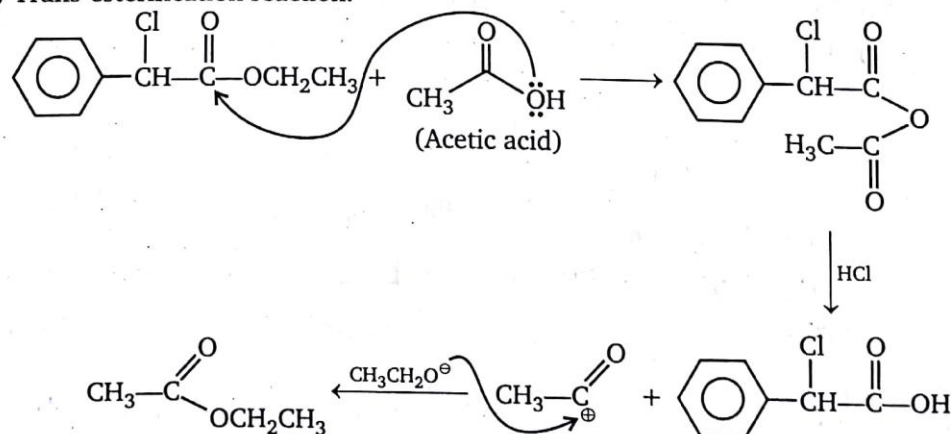
65. (b) By esterification reaction.

$C_6H_5-\underset{OH}{\underset{|}{CH}}-\overset{O}{\overset{||}{C}}-O-Et$ $C_6H_5-\underset{Cl}{\underset{|}{CH}}-CO_2Et$

66. (a) Trans-esterification reaction.

$C_6H_5-\overset{Cl}{\overset{|}{CH}}-\overset{O}{\overset{||}{C}}-OCH_2CH_3$ + CH_3COOH (Acetic acid) ⟶ $C_6H_5-\overset{Cl}{\overset{|}{CH}}-\overset{O}{\overset{||}{C}}-O-\overset{O}{\overset{||}{C}}-CH_3$

$\downarrow$ HCl

$CH_3-\overset{O}{\overset{||}{C}}-OCH_2CH_3$ $\xleftarrow{CH_3CH_2O^{\ominus}}$ $CH_3-\overset{\oplus}{C}=O$ + $C_6H_5-\overset{Cl}{\overset{|}{CH}}-\overset{O}{\overset{||}{C}}-OH$

67. (a) Trans-esterification reaction.

68. (d) In acetylation reaction molecular formula of reactant increase by C_2H_2O.

∴In 3-alcohol ∴molecular formula increases by $C_6H_6O_3$

triol (–OH, –OH, –OH) $\xrightarrow{3Ac_2O}$ (–OAc, –OAc, –OAc)

69. (a) butanal $\xrightarrow[H^+]{CH_3OH}$ hemiacetal (OCH_3, OH) $\xrightarrow[H^\oplus]{CH_3OH}$ (OCH_3, OCH_3) (Acetal)

70. (c) cyclohexanone + $H—C{\equiv}\overset{\ominus}{C}\,\overset{\oplus}{Na}$ ⟶ ($\overset{\ominus}{O}$, $C{\equiv}CH$) $\xrightarrow{H_3O^\oplus}$ (OH, $C{\equiv}CH$)

71. (b) (*A*) (O, CHO) (*B*) (O, CH acetal) (*C*) (OH, CH_3, CHO) (*D*) (OH, CH_3, CH_2—OH)

72. (d) cyclohexene $\xrightarrow{M-CPBA}$ epoxide (O) $\xrightarrow{(i)\ \overset{\ominus}{C}H_3\overset{\oplus}{M}gBr}$ (OH, CH_3) + (OH, CH_3)

73. (d) (Ph, Ph, H, O, H, O) $\xrightarrow[\text{(better than } NaBH_4)]{1.\ LiAlH_4}$ (Ph, Ph, HOH_2C, CH_2OH) $\xrightarrow[\Delta]{H^\oplus}$ (Ph, Ph, O)

$\downarrow$ 2. O_6O_4 (hydroxilation) syn

(Ph, OH, OH, Ph, O) $\xrightarrow[\text{(Periodic acid)}]{3.\ HIO_4}$ (Ph, O, O, Ph, O) $\xrightarrow{4.\ NaBH_4}$ (OH, OH, Ph, Ph, O)

74. (c) (CH_3, Ph, CD_3, :ÖH) $\xrightarrow[S_N1 \text{ reaction}]{H^+}$ (CH_3, $\overset{\oplus}{C}$, Ph, CD_3) $\xrightarrow{Br^\circ}$ Racemisation takes place

75. (b) $Me_2—C(OH)—C(NH_2)Me_2 \xrightarrow{NaNO_2+HCl} Me—C(=O)—CMe_3$

pinacol-diazotization

76. (b) $CH_3—CH(CH_3)—O—Et \xrightarrow{H_3O^+}$ (isopropyl alcohol, OH) $+ EtOH$

(c) $CH_3—C(=CH_2)—OEt \xrightarrow{H^+} CH_3—\overset{\oplus}{C}(CH_3)—OEt \xrightarrow{H_2\ddot{O}:} CH_3—C(\overset{\oplus}{O}H_2)(CH_3)—OEt \longrightarrow CH_3—\overset{\oplus}{C}(CH_3)—:OH + EtOH \xrightarrow{-H^{\oplus}} CH_3—C(=O)—CH_3$

77. (c) $Ph_3C—C(=O)—OH \xrightarrow[CH_3OH]{H^+} Ph_3C—\overset{\oplus}{C}=\ddot{O}: \longrightarrow Ph_3\overset{\oplus}{C} + CO \xrightarrow{CH_3\ddot{O}H} Ph_3C—OCH_3 + H^+$

78. (c) (1-tetralol, OH) $\xrightarrow{TsCl}$ (OTs) (A) $\xrightarrow{LiAlH_4}$ (tetralin) (B)

79. (d) $CH_3—CH(OH)—CH_2CH_3 \xrightarrow{H^+} CH_3—\overset{\oplus}{C}H—CH_2CH_3$ 2° carbocation

$CH_3—C(CH_3)(OH)—CH_2CH_3 \xrightarrow{H^+} CH_3—\overset{\oplus}{C}(CH_3)—CH_2CH_3$ 3° carbocation

Stability order of carbocation 3°>2°

80. (c) Rate can be explained by stability of carbocation.

81. (c) $HO—CH_2CH_2CH_2—C(=CH_2)—CH_2OH \xrightarrow{MnO_2} HO—CH_2CH_2CH_2—C(=CH_2)—CHO$

MnO_2 selectively oxidises allylic alcohol.

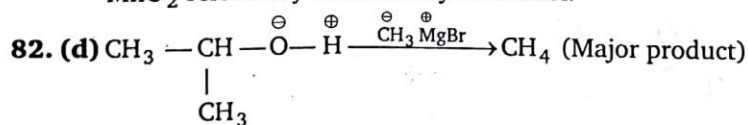
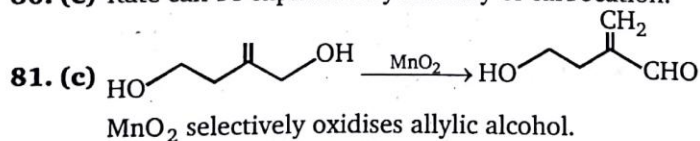
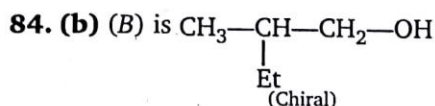
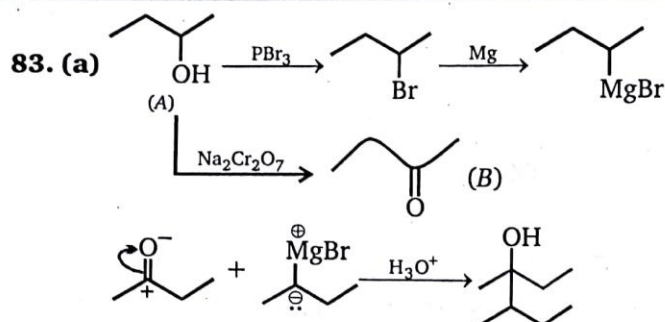
82. (d) $CH_3—CH(CH_3)—\overset{\ominus}{O}—\overset{\oplus}{H} \xrightarrow{\overset{\ominus}{CH_3}\overset{\oplus}{MgBr}} CH_4$ (Major product)

Acid-base reaction takes place.

83. (a) (A) OH $\xrightarrow{PBr_3}$ Br $\xrightarrow{Mg}$ MgBr

(A) $\xrightarrow{Na_2Cr_2O_7}$ (B) (ketone, O)

O^- (+) + $\overset{\oplus}{MgBr}$ ($\ominus$) $\xrightarrow{H_3O^+}$ OH

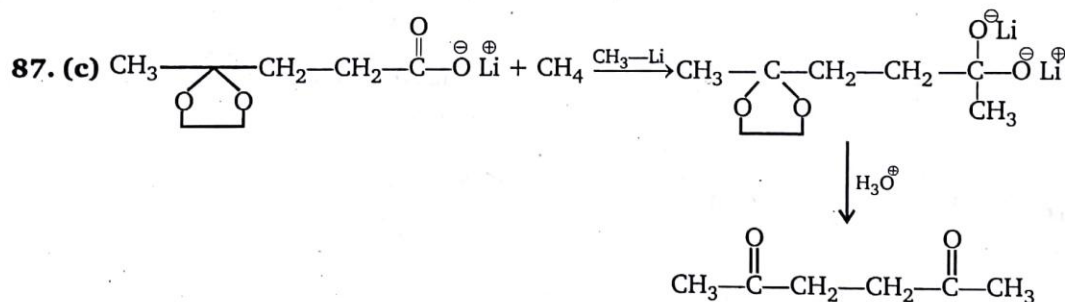
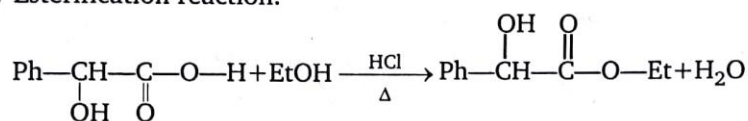
84. (b) (B) is $CH_3—CH(Et)—CH_2—OH$ (Chiral)

85. (b) $NaBH_4$ will not reduces NO_2.

86. (c) Esterification reaction.

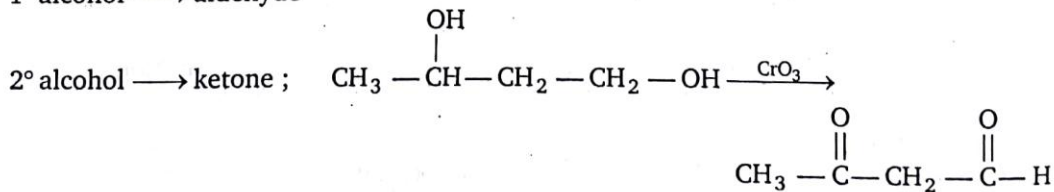
$$Ph—CH(OH)—C(=O)—O—H + EtOH \xrightarrow[\Delta]{HCl} Ph—CH(OH)—C(=O)—O—Et + H_2O$$

87. (c) CH_3—C(ketal, O O)—$CH_2—CH_2—C(=O)—\overset{\ominus}{O}\ \overset{\oplus}{Li}$ + CH_4 $\xrightarrow{CH_3—Li}$ CH_3—C(ketal, O O)—$CH_2—CH_2—C(\overset{\ominus}{O}Li)(CH_3)—\overset{\ominus}{O}\ \overset{\oplus}{Li}$

$\downarrow H_3O^{\oplus}$

$$CH_3—C(=O)—CH_2—CH_2—C(=O)—CH_3$$

88. (b) CrO_3 / pyridine is mild oxidising agent.

1° alcohol ⟶ aldehyde

2° alcohol ⟶ ketone ; $CH_3—CH(OH)—CH_2—CH_2—OH \xrightarrow{CrO_3}$ $CH_3—C(=O)—CH_2—C(=O)—H$

89. (d)

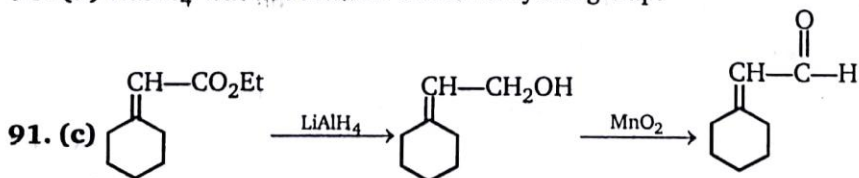
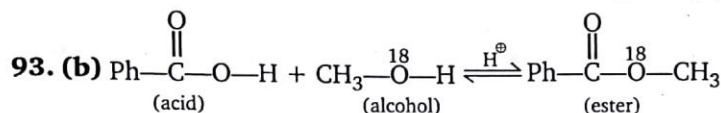
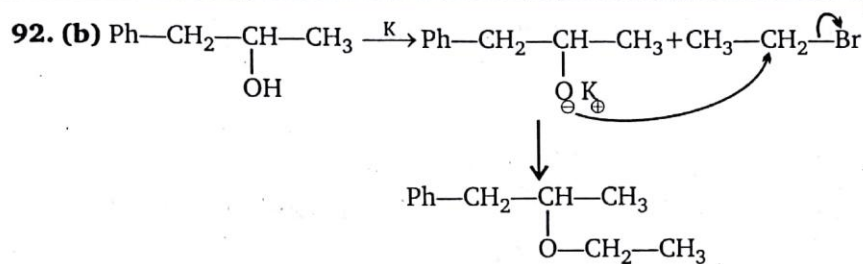
90. (a) $NaBH_4$ will not reduces alkene & cyano group.

91. (c) (cyclohexylidene)$CH—CO_2Et$ $\xrightarrow{LiAlH_4}$ (cyclohexylidene)$CH—CH_2OH$ $\xrightarrow{MnO_2}$ (cyclohexylidene)$CH—C(=O)—H$

92. (b) Ph—CH$_2$—CH(OH)—CH$_3$ $\xrightarrow{K}$ Ph—CH$_2$—CH(O$^{\ominus}$K$^{\oplus}$)—CH$_3$ + CH$_3$—CH$_2$—Br

↓

Ph—CH$_2$—CH(O—CH$_2$—CH$_3$)—CH$_3$

93. (b) Ph—C(=O)—O—H (acid) + CH$_3$—$\overset{18}{O}$—H (alcohol) $\xrightleftharpoons{H^{\oplus}}$ Ph—C(=O)—$\overset{18}{O}$—CH$_3$ (ester)

94. (a) Alcohol shows acidic behavior in esterification, so CH_3OH is most acidic among all the options, so rate of esterification will be maximum.

95. (d) (a) CH$_3$—C(CH$_3$)=CH—CH$_2$—Cl ⟶ CH$_3$—CH(CH$_3$)=CH—$\overset{\oplus}{C}$H$_2$ more stable (Resonance stabilised)

R—Cl ⟶ $R^{\oplus}$ less stable

(b) CH$_3$—CH=CH—CH$_2$OH $\xrightarrow{H^{\oplus}}$ CH$_3$CH=CH—$\overset{\oplus}{C}$H$_2$ ⟷ CH$_3$—$\overset{\oplus}{C}$H—CH=CH$_2$

1° (less stable) $\xrightarrow{Br^-}$ Minor; 2° (more stable) $\xrightarrow{Br^-}$ Major

(c) CH$_3$—CH(:ÖH)—CH=CH$_2$ $\xrightarrow{H^+}$ CH$_3$—$\overset{\oplus}{C}$H—CH=CH$_2$ ⟷ CH$_3$—CH=CH—$\overset{\oplus}{C}$H$_2$

$\xrightarrow{H_2\ddot{O}:}$ CH$_3$—CH(OH)—CH=CH$_2$ (1-butene-3-ol)

$\xrightarrow{H_2\ddot{O}:}$ CH$_3$—CH=CH—CH2OH (2-buten-1-ol)

96. (b) 1-(hydroxymethyl)cyclohexan-1-ol (OH, OH, CH$_2$) $\xrightarrow{HIO_4}$ cyclohexanone $\xrightarrow{LiAlH_4}$ cyclohexanol (OH)

97. (c) H$_2$C=CH—CH$_2$—CH$_2$—CH(OH)—CH$_3$ $\xrightarrow[Pyridine]{SOCl_2}$ H$_2$C=CH—CH$_2$—CH$_2$—CH(Cl)—CH$_3$

$\xrightarrow{O_3/Zn\ (H_2O)}$ H—C(=O)—CH$_2$—CH$_2$—CH(Cl)—CH$_3$ $\xrightarrow{NaBH_4}$ HO—CH$_2$—CH$_2$—CH$_2$—CH(Cl)—CH$_3$

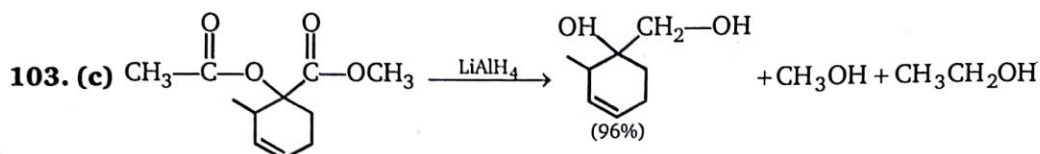
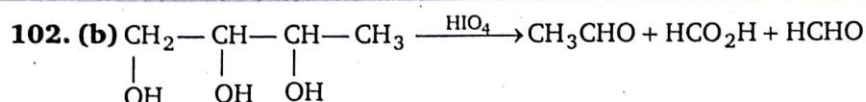
98. (a) 2-Butanol

99. (c) $LiAlH_4$

100. (a) cyclohexyl—CH$_2$—OH

101. (d) 3° alcohol not oxidised.

102. (b) $CH_2(OH)-CH(OH)-CH(OH)-CH_3 \xrightarrow{HIO_4} CH_3CHO + HCO_2H + HCHO$

103. (c) $CH_3-\overset{O}{\overset{\|}{C}}-O$ (ring) $\overset{O}{\overset{\|}{C}}-OCH_3 \xrightarrow{LiAlH_4}$ (ring with OH and CH_2-OH) (96%) $+ CH_3OH + CH_3CH_2OH$

104. (c) Alkoxide group of ester is replace by alkoxy group of alcohol, is known as trans esterification.

C — C(OH) — C — C

105. (d) $CH_3-CH(CH_3)-CH_2-OH \xrightarrow{PBr_3} CH_3-CH(CH_3)-CH_2-Br \xrightarrow{Mg} CH_3-CH(CH_3)-\overset{\delta\ominus}{C}H_2MgBr$ + (epoxide)

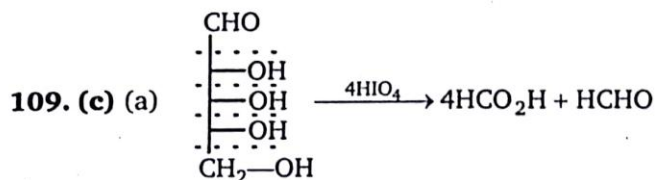
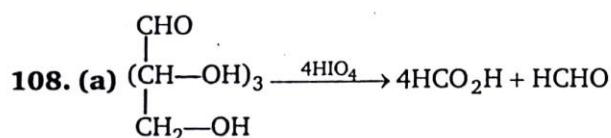
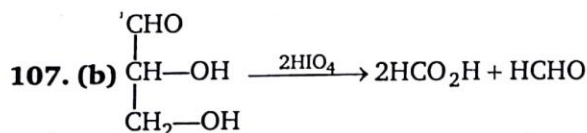
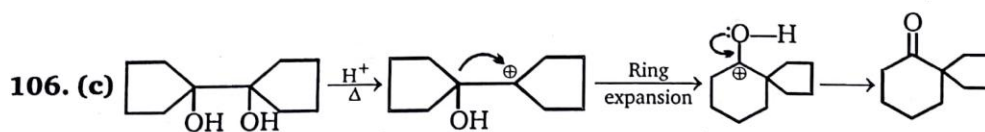
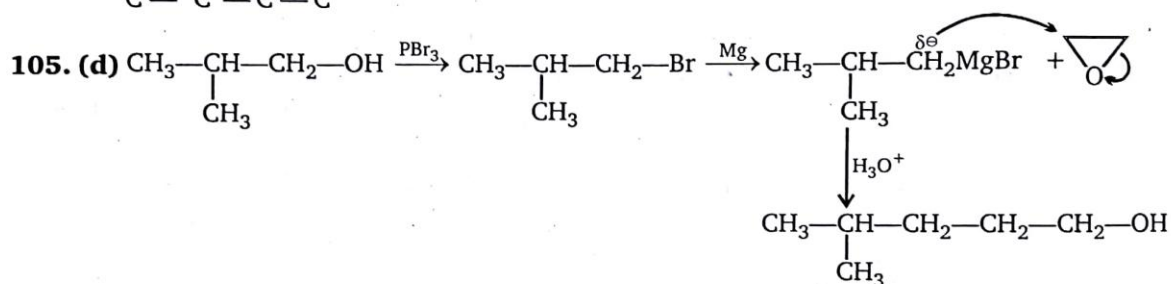
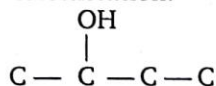
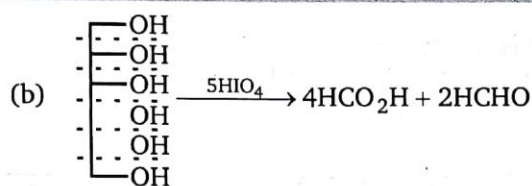
$\xrightarrow{H_3O^+} CH_3-CH(CH_3)-CH_2-CH_2-CH_2-OH$

106. (c) (cyclopentyl diol, OH OH) $\xrightarrow[\Delta]{H^+}$ (carbocation, OH) $\xrightarrow{\text{Ring expansion}}$ (:O—H, ⊕) $\longrightarrow$ (spiro ketone)

107. (b) $CHO-CH(OH)-CH_2-OH \xrightarrow{2HIO_4} 2HCO_2H + HCHO$

108. (a) $CHO-(CH-OH)_3-CH_2-OH \xrightarrow{4HIO_4} 4HCO_2H + HCHO$

109. (c) (a) CHO, —OH, —OH, —OH, CH_2-OH $\xrightarrow{4HIO_4} 4HCO_2H + HCHO$

(b) OH, OH, OH, OH, OH, OH (six-carbon chain) $\xrightarrow{5HIO_4}$ $4HCO_2H + 2HCHO$

Ratio of formic acid $= \frac{4}{4} = 1$

110. (d) CHO–C(=O)–CH(OH)–CH_2–OH $\xrightarrow{3HIO_4}$ $2HCO_2H + CO_2 + HCHO$

111. (c) $H_2C{=}CH{-}CH(C_6H_5){-}CH_3 \xrightarrow{H^{\oplus}} CH_3{-}\overset{\oplus}{C}H{-}CH(C_6H_5){-}CH_3$

2° carbocation (less stable)

$\downarrow$ 1,2 $H^{\ominus}$ shift

$CH_3{-}CH_2{-}\overset{\oplus}{C}(C_6H_5){-}CH_3$

3° carbocation (more stable)

$\xrightarrow{H_2\ddot{O}:}$ $CH_3CH_2{-}C(C_6H_5)(OH){-}CH_3$

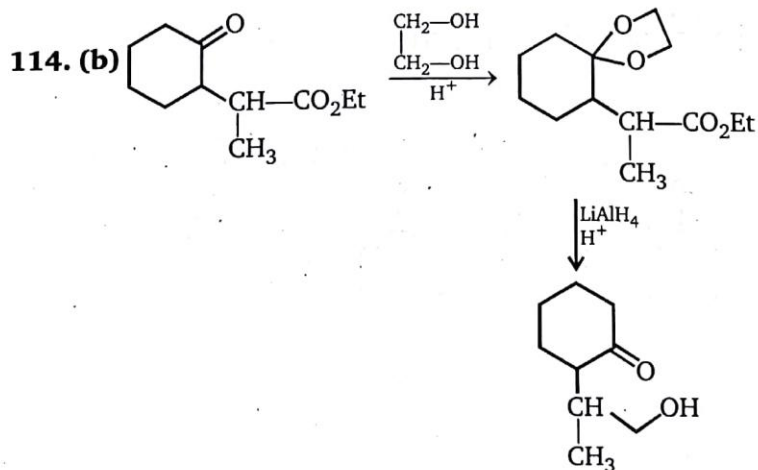
2 Phenyl butan-2 ol (major product)

112. (b) (sodium salicylate: COONa, OH on benzene ring) $\xrightarrow[CaO]{NaOH +}$ (phenol) $+ Na_2CO_3$

113. (b) $(x = 2)$ HIO_4 will not cleave ether.

114. (b) (2-substituted cyclohexanone with $CH(CH_3){-}CO_2Et$) $\xrightarrow[H^+]{CH_2{-}OH,\ CH_2{-}OH}$ (cyclic ketal, with $CH(CH_3){-}CO_2Et$)

$\downarrow$ $LiAlH_4$, H^+

(cyclohexanone with $CH(CH_3){-}CH_2OH$)

ketone is more reactive than ester toward nucleophilic attack.

115. (b) CH_2—O—H / CH_2—O—H + Cl—C(=O)—Cl ⟶ CH_2—OH / CH_2—O—C(=O)—Cl ⟶ cyclic carbonate (ethylene carbonate, C=O)

116. (d) 4-(CO_2CH_3)cyclohexanone $\xrightarrow[(A)]{CH_2-OH / CH_2-OH}$ ketal with CO_2CH_3 $\xrightarrow[(B)]{LiAlH_4}$ ketal with CH_2OH $\xrightarrow[CrO_3/CH_2Cl_2 \text{ (mild)}]{(C)}$ ketal with CHO

$(D) = H_3O^{\oplus}$ ⟶ O= cyclohexane —CHO

117. (b)

118. $CH_3—CH_2—OH \xrightarrow{PCl_5} CH_3—CH_2Cl + POCl_3 + HCl$

$\downarrow AgNO_2$

$CH_3CH_2—NO_2$

119. (b) $CH_3 \text{-}(CH_2)_3\text{-} \ddot{O}H + CH_3—S(=O)_2—Cl \xrightarrow{Et_3N} CH_3\text{-}(CH_2)_3\text{-} O—S(=O)_2—CH_3$ (A)

$\downarrow K^{14}CN \ (SN_2)$

$CH_3\text{-}(CH_2)_3\text{-} {}^{14}COOH \xleftarrow{H_3O^{\oplus}} CH_3\text{-}(CH_2)_3\text{-} {}^{14}CN$ (B)

120. (a)

(a) Phenol (OH) $\xrightarrow{\text{1. Na metal}}$ phenoxide ($O^{\ominus}$) $\xrightarrow[\text{(Polar, aprotic solvent)}]{CH_3CH_2CH_2Br}$ Ph—O—$CH_2CH_2CH_3$

(b) H_3C—CH_2—CH_2—OH $\xrightarrow{\text{1. Na metal}}$ H_3C—CH_2—CH_2—$O^{\ominus}$ + bromobenzene (:Br:) (d.b.c) No SN_2 because of

(c) Anisole ($C_6H_5-O-CH_3$) $\xrightarrow{\text{1. Na metal}}$ no reaction

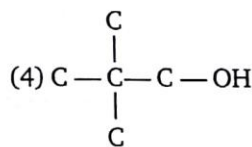
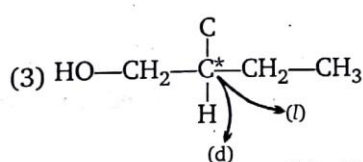
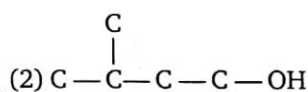
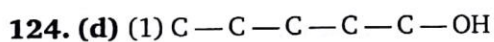
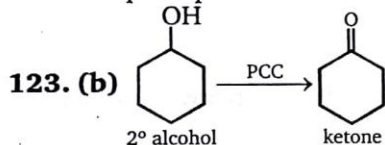
(d) $H_3C-CH_2-CH_2-C_6H_4-OH$ $\xrightarrow[\text{2. HBr}]{\text{1. Na metal}}$ $H_3C-CH_2-CH_2-C_6H_4-OH$

121. (a) 3-(hydroxymethyl)cyclohexanol [OH (2°), OH (1°)] $\xrightarrow{\text{Oxidation}}$ 3-oxocyclohexanecarboxylic acid [O (ketone), HO–C(=O) (Acid)]

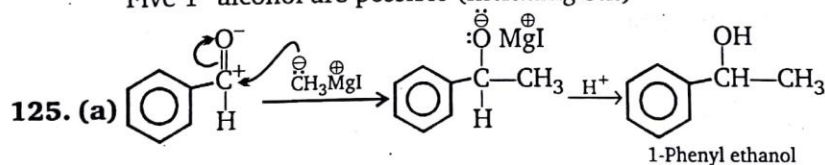
122. (b) Removal of water shift the org. reaction into forward direction according to Le-chatelier's principle.

123. (b) Cyclohexanol (2° alcohol) $\xrightarrow{\text{PCC}}$ Cyclohexanone (ketone)

124. (d) (1) C—C—C—C—C—OH (2) C—C(C)—C—C—OH

(3) $HO-CH_2-\overset{*}{C}H(C)-CH_2-CH_3$ (d), (l) (4) C—C(C)(C)—C—OH

Five 1° alcohol are possible (Including S.I.)

125. (a) C_6H_5-CHO $\xrightarrow{\overset{\ominus}{C}H_3\overset{\oplus}{M}gI}$ $C_6H_5-CH(\overset{\ominus}{O}\overset{\oplus}{M}gI)-CH_3$ $\xrightarrow{H^+}$ $C_6H_5-CH(OH)-CH_3$

1-Phenyl ethanol

126. (c) 92g of a compound react with excess of CH_3MgI to give $x \times 22400$ mL of CH_4 at STP.

1 g of a compound react with excess of CH_3MgI to give $\frac{x \times 22400}{92}$

0.092 of a compound react with excess of CH_3MgI to give $\frac{x \times 22400}{92} \times 0.092$

$$\frac{x \times 22400 \times 0.092}{92} = 67 \text{ mL of } CH_4 \text{ at STP}$$

$$x = \frac{67 \times 92}{22400 \times 0.092} = \frac{67 \times 92 \times 1000}{22400 \times 92} = \frac{670}{224} = 2.99 \approx 3$$

$x \Rightarrow$ number of active hydrogen in compound.

active $H \Rightarrow 3$

127. (b) Migratory aptitude $\propto e^-$ density in benzene ring

p-anisyl (OMe) (a) > p-tolyl (Me) (d) > phenyl (b) > p-chlorophenyl (Cl) (c)

128. (c) (tetrahydropyranyl ether, $-O-CH_2R$) $\xrightarrow{H^+}$ (ring O protonated) $\longrightarrow$ (ring-opened OH, oxocarbenium $\overset{\oplus}{O}$) $\longrightarrow$ (OH, COH) $+ RCH_2OH$

129. (d) Me–C(Et)(H)–OH $\xrightarrow[\text{(ii)LiBr}]{\text{(i)TsCl/Py}}$ Br–C(Et)(H)–Me

(R)-2-Butanol → (R)-2-Butyl Bromide

Reaction with TsCl follows retention whereas with LiBr it follows inversion of configuration.

130. (a) $CH_3-\overset{*}{C}H(:\ddot{O}H)-(CH_2)_5-CH_3 \xrightarrow{\text{dil. acid}} CH_3-CH=CH-(CH_2)_4-CH_3$

2-octanol (optically active)

dehydration of alcohol takes place in dil. acid and alkene is produced which shows G.I.

131. (c) 2-Methyl butanoic acid + 2-Butanol $\xrightleftharpoons{\text{esterification}}$ ester + H_2O

(±) (±)

↓

possible configuration of ester will be

↓

ester consist of two stereo centres

↓

chiral center during whole reaction not affected that's why all esters are optically active.

132. (b) Cyclopentanol $\xrightarrow{PBr_3}$ bromocyclopentane (W) $\xrightarrow{Mg/ether}$ cyclopentyl-MgBr (X) $\xrightarrow{(V)/ether}$ $\overset{\ominus}{O}\overset{\oplus}{Mg}Br$ adduct $\xrightarrow{H_3O^+}$ (Y) $\xrightarrow{CH_3-\overset{O}{\overset{\|}{C}}-Cl}$ (Z) $O-\overset{O}{\overset{\|}{C}}-CH_3$

Cyclopentanol $\xrightarrow{Na_2Cr_2O_7}$ cyclopentanone (V)

133. (c) $Ph-\underset{:\ddot{O}H}{\overset{H}{C}}-Ph \xrightarrow{AlCl_3} Ph-\overset{\oplus}{C}H-Ph$ ($H-O-\overset{\ominus}{Al}Cl_3$) $\xrightarrow{\overset{\ominus}{H}} Ph-CH_2-Ph$

134. (b) $OEt-\underset{}{\overset{OEt}{CH}}-\overset{\ddot{O}:}{\overset{\|}{C}}-H \xrightarrow[(ii)H_3O^+]{(i)\overset{\ominus}{C}H_3\overset{\oplus}{Mg}I} OEt-\overset{OEt}{CH}-\underset{CH_3}{\overset{O-H}{C}}-H \xrightarrow{H_3O^+} HO-\overset{OH}{CH}-\underset{OH}{CH}-CH_3$

$\xrightarrow{-H_2O} H-\overset{O}{\overset{\|}{C}}-\underset{OH}{CH}-CH_3$ (A)

135. (a) Reaction (1) $CH_3-CH=CH-CH_3 \xrightarrow[\text{Reagent}]{\text{Baeyer's}} CH_3-\underset{OH}{CH}-\underset{OH}{CH}-CH_3$ (A) $\xrightarrow{NaIO_4} 2CH_3CHO$

Reaction (2) $CH_3-CH=CH-CH_3 \xrightarrow[\text{Leumix Reagent}]{KMnO_4/NaIO_4} 2CH_3COOH$

136. (c) 1-Tetralol (OH) $\xrightarrow{TsCl}$ (A) (OTs) $\xrightarrow{LiAlH_4}$ tetralin

137. (d) Cyclohexene:

- $\xrightarrow{O_3,\ Zn+H_2O}$ OHC–(CH$_2$)$_4$–CHO $\xrightarrow{LiAlH_4}$ CH_2—OH / CH_2—OH (diol)
- $\xrightarrow{O_3/H_2O_2}$ HOOC–(CH$_2$)$_4$–COOH $\xrightarrow{LAH}$ CH_2—OH / CH_2—OH
- $\xrightarrow{\text{Cold dil. } KMnO_4}$ cis-diol (OH, OH) $\xrightarrow{HIO_4}$ CHO / CHO $\xrightarrow{LAH}$ CH_2OH / CH_2OH

138. (d) (a) CH_3-cyclohexenol (:ÖH) $\xrightarrow{H^+}$ $^{\oplus}OH_2$ $\longrightarrow$ $\oplus$ $\longrightarrow$ $\oplus$ $\longleftrightarrow$ $\oplus$ (tertiary allylic) $\xrightarrow{Cl^-}$ 1-chloro-1-methylcyclohexene derivative (CH_3, Cl)

Rearrangement takes place.

(b) CH_3-cyclohexenol (ÖH) $\xrightarrow{H^+}$ CH_3 $\oplus$ $\longleftrightarrow$ CH_3 $\oplus$ $\xrightarrow{Cl^-}$ CH_3, Cl product

(c) CH_3, OH (tertiary allylic alcohol) $\xrightarrow{H^+}$ CH_3 $\oplus$ $\longrightarrow$ CH_3, Cl product

139. (b) Cyclohexene $\xrightarrow[\text{(Per acid)}]{R—\overset{\overset{\alpha}{O}}{\overset{\|}{C}}—\overset{\beta}{O}—\overset{\gamma}{O}—H}$ epoxide (Ö:) $\xrightarrow[\text{(ii) } H_3O^+]{\text{(i)} \overset{\ominus}{C}H_3\overset{\oplus}{M}gBr}$ trans-2-methylcyclohexanol (OH, CH_3)

140. (d) Chiral center is not affected during the reaction so change in sign of rotation is merely a coincidence.

141. (c) Wittig Reaction:

$C_6H_{11}-C(=O)-CH_3$ + $\overset{\oplus}{P}(Ph)_3-\overset{\ominus}{C}H-CH_2CH_3$ ⟶ $C_6H_{11}-C(CH_3)(O-P(Ph)_3)-CH-CH_2CH_3$ ⟶ cyclic four membered T.S. ⟶ $O=P(Ph)_3$ + $C_6H_{11}-C(CH_3)=CH-CH_2CH_3$

$\xrightarrow{(i)\ B_2H_6,\ (ii)\ CH_3COOH}$ $C_6H_{11}-CH(CH_3)-CH_2CH_2CH_3$

b = breaking
f = forming

142. (b) β-keto ester (2-oxocyclohexane-COOEt) $\xrightarrow{H_3O^+}$ β-keto acid (COOH) ⟶ cyclohexanone + $CO_2\uparrow$

decarboxylation takes place

143. (b) Cyclobutane(COOEt)$-C(=O)-CH_3$ $\xrightarrow{H_3O^+}$ Cyclobutane(COOH)$-C(=O)-CH_3$ (β-keto acid) $\xrightarrow{\Delta}$ Cyclobutyl$-C(=O)-CH_3$ $\xrightarrow{I_2^+ / NaOH}$ Cyclobutyl$-\overset{\ominus}{C}OO\overset{\oplus}{Na}$ + CHI_3

144. (d) $R-CH(OH)-R \xrightarrow{CrO_3} R-C(=O)-R$

2° alcohol ⟶ ketone

145. (b) (S) Carboxylic acid + (R+S) alcohol ⇌ RS + SS ← configuration of ester

a mixture of diastereomers are produced.

146. (c) EtOOC, COOEt, O, O $\xrightarrow{H_3O^+}$ HOOC, COOH, O, O (β-keto acid) $\xrightarrow[-2CO_2]{O}$ O, O (keto form) ⇌ OH, OH (enol form stable)

147. (b) Reaction is an example of nucleophilic addition

Rate of NAR acid halide>ald.>ketone>acid

148. (a) O, NH_2 $\xrightarrow{LiAlH_4}$ $\ddot{N}H_2$ (1° amine) $\xrightarrow{CHCl_3+KOH}$ $N \equiv C$ (Isocyanide)

149. (d) SBH can't reduce ester and acid.

150. (a) Number of Hydroxyl group $n = \frac{m' - m}{42}$

Where m' = mass of product

m = unknown compound

$n = \frac{390 - 180}{42} = 5$

151. (c) For a compound to give $NaHCO_3$ test positive, it must be more acidic than H_2CO_3 ($pKa = 6.4$)

And for a compound to give NaOH test positive, it must be more acidic than H_2O ($pKa = 15.7$)

For $NaHCO_3$ as well as by NaOH

		NaOH	$NaHCO_3$
(a)	COOH (benzoic acid), OH (phenol)	×	✓
(b)	OH (phenol), CH_2OH (benzyl alcohol)	×	×

(c) COOH CH$_2$OH ✓ ✓

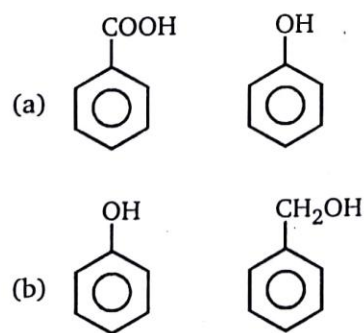
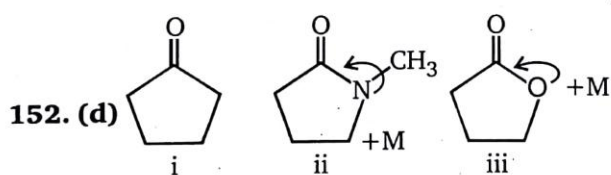
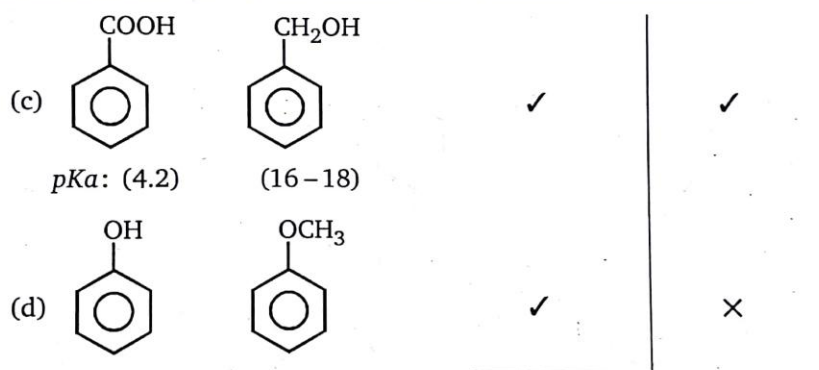
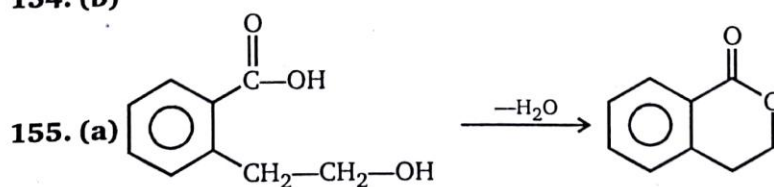
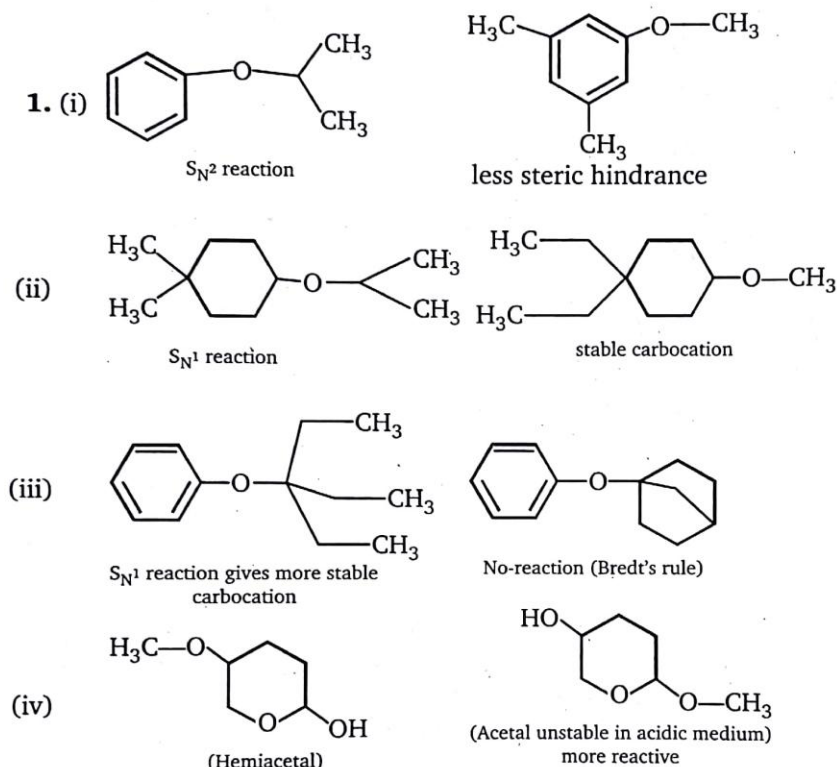
pKa: (4.2) (16 – 18)

(d) OH OCH$_3$ ✓ ×

152. (d)

153. (b)

154. (b)

155. (a)

Level-2

2. (A) d (due to formation of most stable carbocation)

(B) a, c, e, f, g, h (less stable carbocation converted into more stable)

(C) a, b, c (cis and trans-2-pentene)

(D) d (3° alcohol is least acidic) Due to $+I$ effect of three methyl groups.

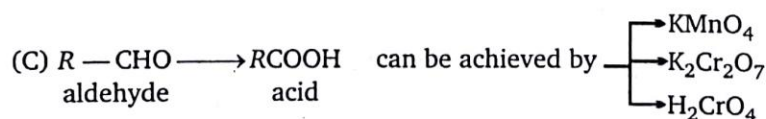
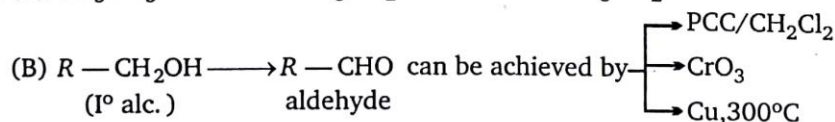
(E) d, e, f, g, h (Due to increase in number of α –(H))

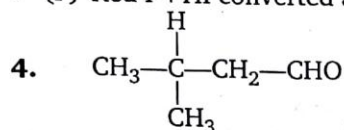
(F) e, f, g, h (under go rearrangement) because less stable carbocation converted to more stable carbocation.

3. (A) $CH_3CH_3 \xrightarrow{Br_2/h\nu} CH_3CH_2Br \xrightarrow{aq.KOH} CH_3CH_2OH$

(B) $R-CH_2OH \longrightarrow R-CHO$ can be achieved by → PCC/CH_2Cl_2, → CrO_3, → Cu,300°C
(I° alc.) aldehyde

(C) $R-CHO \longrightarrow RCOOH$ can be achieved by → $KMnO_4$, → $K_2Cr_2O_7$, → H_2CrO_4
aldehyde acid

(D) $R-COOH \longrightarrow R-CHO$ DIBAL—H Reduces oic acid to aldehyde

(E) LAH, NBH and H_2/N reduces ald. to alcohol.
(F) Red P+HI converted alcohol in to alkene.

4. $CH_3-C(H)(CH_3)-CH_2-CHO$

(a) (T) (b) F (c) due to presence of α-H (True).
(d) (F) ($LiAlH_4$ reduces aldehyde in to alcoholic group)

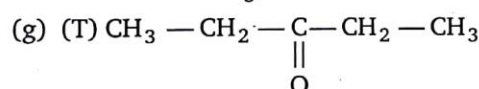
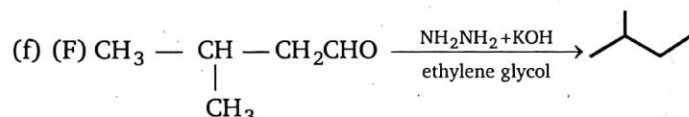
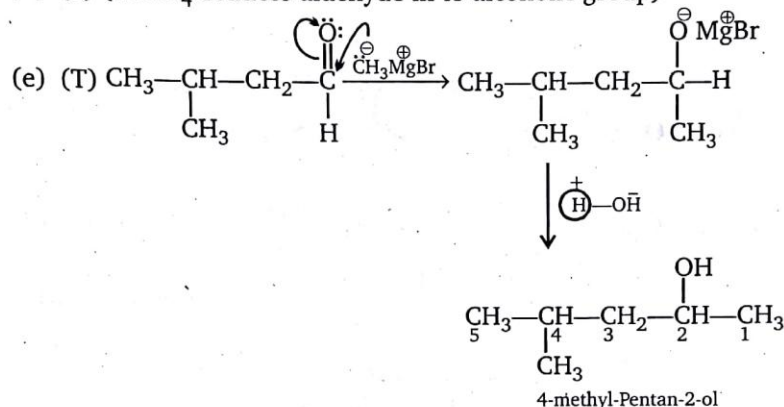
(e) (T) $CH_3-CH(CH_3)-CH_2-CH=O \xrightarrow{\overset{\ominus}{C}H_3\overset{\oplus}{Mg}Br} CH_3-CH(CH_3)-CH_2-C(\overset{\ominus}{O}\overset{\oplus}{Mg}Br)(H)(CH_3)$

$\downarrow \overset{+}{H}-\bar{O}H$

$\underset{5}{CH_3}-\underset{4}{CH}(CH_3)-\underset{3}{CH_2}-\underset{2}{CH}(OH)-\underset{1}{CH_3}$

4-methyl-Pentan-2-ol

(f) (F) $CH_3-CH(CH_3)-CH_2CHO \xrightarrow[\text{ethylene glycol}]{NH_2NH_2+KOH}$ (2-methylbutane, skeletal)

(g) (T) $CH_3-CH_2-C(=O)-CH_2-CH_3$

3-pentanone is function group isomer of 3-methyl butanal.

5. (1) $C_6H_5-CH_2-OH \xrightarrow[(3)\ H_3O^{(+)}]{(1)\ \text{Reagent } \boxed{3}\ (2)\ \text{Reactant } \boxed{D}} C_6H_5-CH_2-O-CH_2-CH_2-OH$ ($C_9H_{12}O_2$)

$\xrightarrow[\text{(oxidation)}]{\text{Reagent } \boxed{2}} C_6H_5-CH_2-O-CH_2-CHO$

(2) Reactant $\boxed{C} \xrightarrow{\text{Reagent } \boxed{1}} CH_3-CH_2-C(=O)-O-H$ ($C_3H_6O_2$) $\xrightarrow[\text{(2) Reactant } \boxed{A}\ \text{Reagent } \boxed{7}\ \text{heat}]{\text{(1) Reagent } \boxed{5}}$ +& $C_6H_5-C(=O)-CH_2-CH_3$

(Friedal-Craft reaction)

(3) Cyclopentyl–OH $\xrightarrow[\text{(3)}CO_2 \quad \text{(4)}H_3O^{(+)}]{\text{(1)Reagent [6]} \quad \text{(2)Reagent [8]}}$ Cyclopentyl–C(=O)–O–H ($C_6H_{10}O_2$)

$\xrightarrow[\text{heating with catalytic acid}]{\text{Reactant [C]}}$ Cyclopentyl–C(=O)–O–$CH_2CH_2CH_3$

(Esterification)

(4) Reactant [C] $\xrightarrow{\text{Reagent [2]}}$ C_3H_6O $\xrightarrow[\text{(3)Reactant [F]}]{\text{(1)NaOH solution} \quad \text{(2)Reagent [4]}}$ (product with $OCOCH_3$ and $OCOCH_3$ groups)

$CH_3-CH_2-CHO \xrightarrow[\text{aldol}]{NaOH} CH_3-CH_2-\underset{OH}{CH}-\underset{CHO}{CH}-CH_3 \xrightarrow{NaBH_4} CH_3-\underset{O}{\overset{}{C}}-O-\underset{O}{C}-CH_3$

(esterification)

(5) Reactant [B] $\xrightarrow[\text{(2)Reagent [6]}]{\text{(1)Reagent [4]}}$ C_3H_7Br $\xrightarrow[\text{(3)}H_3O^{(+)}]{\text{(1)Reagent [8]} \quad \text{(2)Reactant [E or F]}}$ (triisopropyl carbinol)–OH

B = acetone (CH_3COCH_3); C_3H_7Br = 2-bromopropane

6. $CH_3-\underset{O}{\overset{}{C}}-\overset{CH_3}{CH}-CH_3$ 3-methyl-2-butanone

(a) (F)$CH_3-\overset{OH}{\underset{CH_3}{C}}-CH_2CH_3 \xrightarrow{(O)}$ Hardly oxidised.

(3° alcohol)

(b) (T) $CH_3-\overset{O}{C}-\underset{CH_3}{CH}-CH_3 \xrightarrow{NaBH_4} CH_3-\overset{OH}{CH}-\underset{CH_3}{CH}-CH_3$

(2° alcohol)

(c) (T) $HC\equiv C-CH(CH_3)-CH_3 \xrightarrow[H_3O^+]{Hg^+} H-C(H)=C(OH)-CH(CH_3)-CH_3$

3-methyl-1-Butyne; enol (unstable)

$\rightleftharpoons CH_3-C(=O)-CH(CH_3)-CH_3$ keto (stable)

(d) (F) (Ketones does not gives Tollen's test)

(e) (T) $HO-CH_2-CH_2-CH_2-CH=CH_2$ Isomer of 3-methyl-2-Butanone

7. $C_6H_5-CH_2-{}^{*}C(H)(OH)-CH_3$

1-Phenyl-2-Propanol

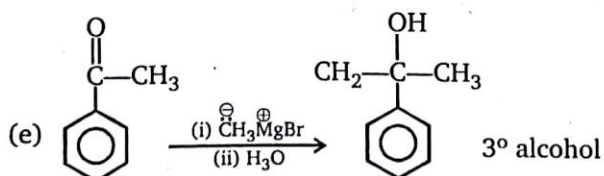
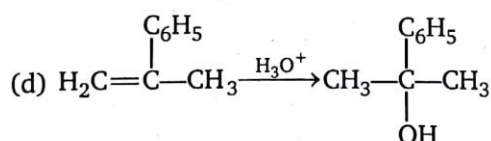
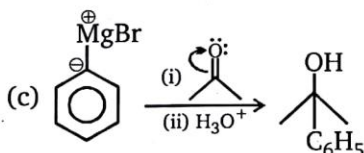
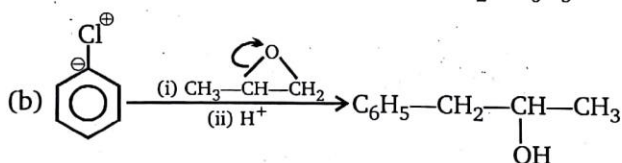
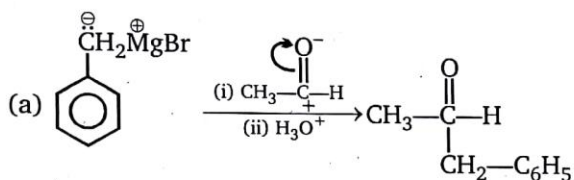
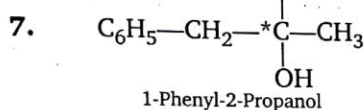
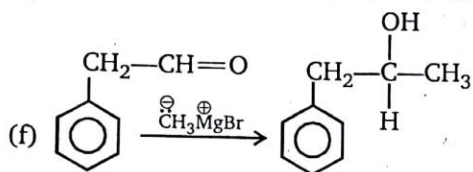
(a) $C_6H_5\overset{\ominus}{C}H_2\overset{\oplus}{M}gBr \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } CH_3-C(=O)-H} CH_3-C(=O)(-H)-CH_2-C_6H_5$

(b) $C_6H_5^{\ominus}Cl^{\oplus} \xrightarrow[\text{(ii) } H^+]{\text{(i) } CH_3-CH-CH_2 \text{ (epoxide)}} C_6H_5-CH_2-CH(OH)-CH_3$

(c) $C_6H_5^{\ominus}\overset{\oplus}{M}gBr \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) acetone}} (CH_3)_2C(OH)C_6H_5$

(d) $H_2C=C(C_6H_5)-CH_3 \xrightarrow{H_3O^+} CH_3-C(C_6H_5)(OH)-CH_3$

(e) $C_6H_5-C(=O)-CH_3 \xrightarrow[\text{(ii) } H_3O]{\text{(i) } \overset{\ominus}{C}H_3\overset{\oplus}{M}gBr} C_6H_5-C(OH)(CH_2)-CH_3$ 3° alcohol

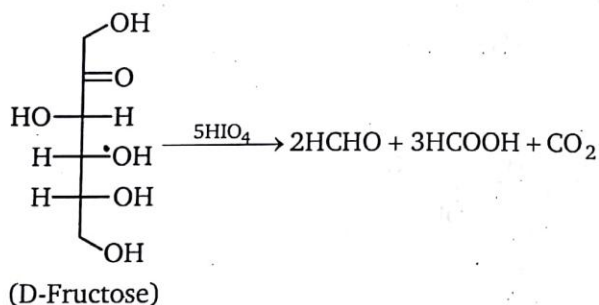
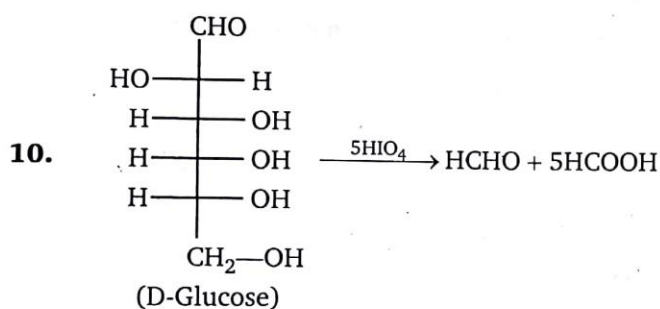
(f) $C_6H_5-CH_2-CH=O \xrightarrow{\overset{\ominus}{C}H_3\overset{\oplus}{Mg}Br} C_6H_5-CH_2-CH(OH)-CH_3$

8. Result of all the reaction is $CH_3-\overset{O}{\overset{\|}{C}}-C\lessdot$ Pinacolone

9. (a) S_{N^1} (b) S_{N^2} (c) S_{N^1} then S_{N^2} (d) S_{N^2}

10. D-Glucose (CHO; HO–C–H; H–C–OH; H–C–OH; H–C–OH; CH_2–OH) $\xrightarrow{5HIO_4}$ $HCHO + 5HCOOH$

(D-Glucose)

D-Fructose (CH_2OH; C=O; HO–C–H; H–C–OH; H–C–OH; CH_2OH) $\xrightarrow{5HIO_4}$ $2HCHO + 3HCOOH + CO_2$

(D-Fructose)

11. (A) II^{nd} step (R.D.S.)

(B) (b) 2 products are formed during reaction

$OH-C(Et)_2-\overset{\oplus}{C}(Ph)_2 \xrightarrow[\text{shift}]{Et^{\ominus}} H\ddot{O}-\overset{\oplus}{C}(Et)-C(Ph)_2-Et \longrightarrow$ $Et-\overset{O}{\overset{\|}{C}}-C(Ph)_2-Et$ Product ... (1)

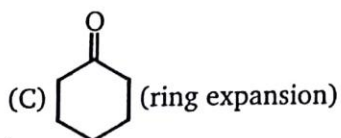
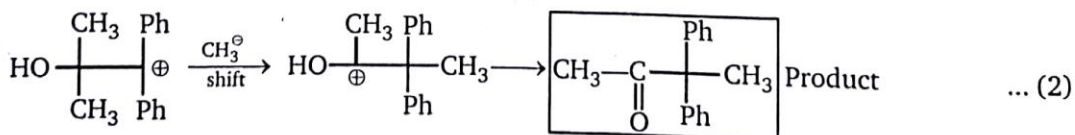
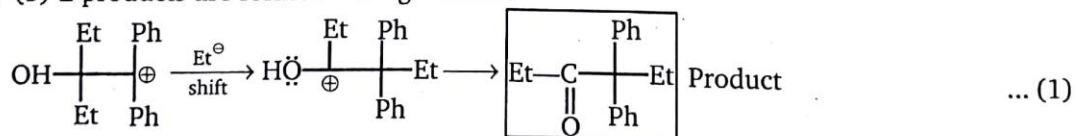
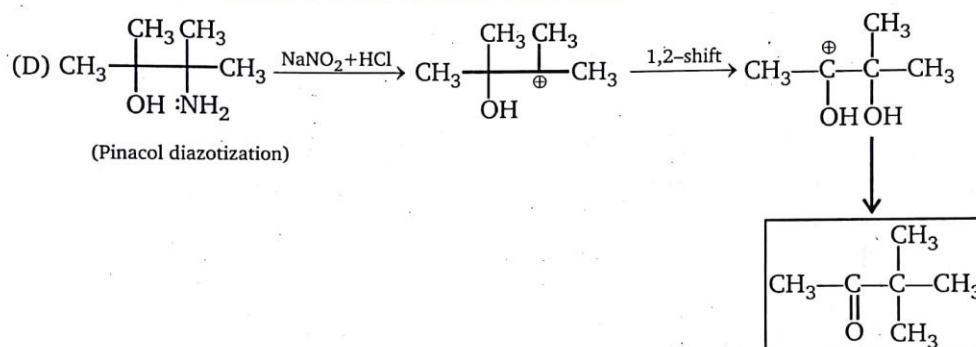
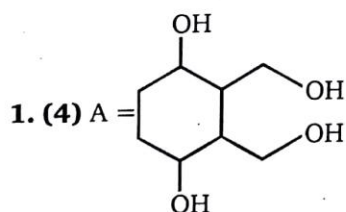
$HO-C(CH_3)_2-\overset{\oplus}{C}(Ph)_2 \xrightarrow[\text{shift}]{CH_3^{\ominus}} HO-\overset{\oplus}{C}(CH_3)-C(Ph)_2-CH_3 \longrightarrow$ $CH_3-\overset{O}{\overset{\|}{C}}-C(Ph)_2-CH_3$ Product ... (2)

(C) Cyclohexanone (ring expansion)

(D) $CH_3-C(CH_3)(OH)-C(CH_3)(\ddot{N}H_2)-CH_3 \xrightarrow{NaNO_2+HCl} CH_3-C(CH_3)(OH)-\overset{\oplus}{C}(CH_3)-CH_3 \xrightarrow{1,2\text{-shift}} CH_3-\overset{\oplus}{C}(OH)-C(CH_3)(OH)-CH_3 \longrightarrow$ $\boxed{CH_3-\underset{\underset{O}{\|}}{C}-C(CH_3)_2-CH_3}$

(Pinacol diazotization)

SUBJECTIVE PROBLEMS

1. (4) A = cyclohexane ring bearing two OH groups (at positions 1 and 4) and two CH_2OH groups (at adjacent positions 2 and 3)

No. of alcohol = No. of moles of Ac_2O consumed.
= 4

7 Aldehydes and Ketones

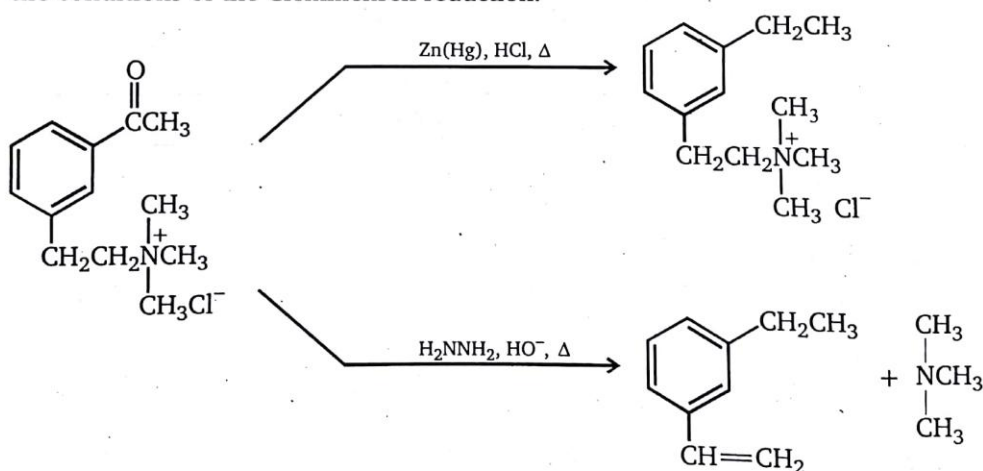
Level-1

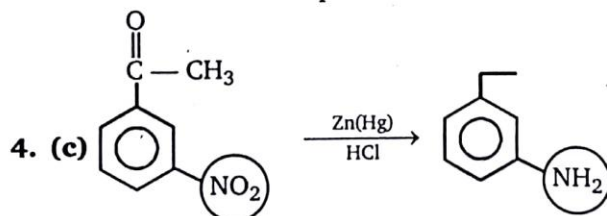
1. (a) Wolff-Kishner as well as SNAr both reaction take place.

2. (b) Quaternary ammonium ion shown below would undergo a Hoffmann elimination reaction under the basic conditions required for the Wolff-Kishner reduction, but it would be inert to the conditions of the Clemmensen reduction.

Starting compound (benzene ring with $\overset{O}{\overset{\|}{C}}CH_3$ and $CH_2CH_2\overset{+}{N}(CH_3)_3\ Cl^-$):

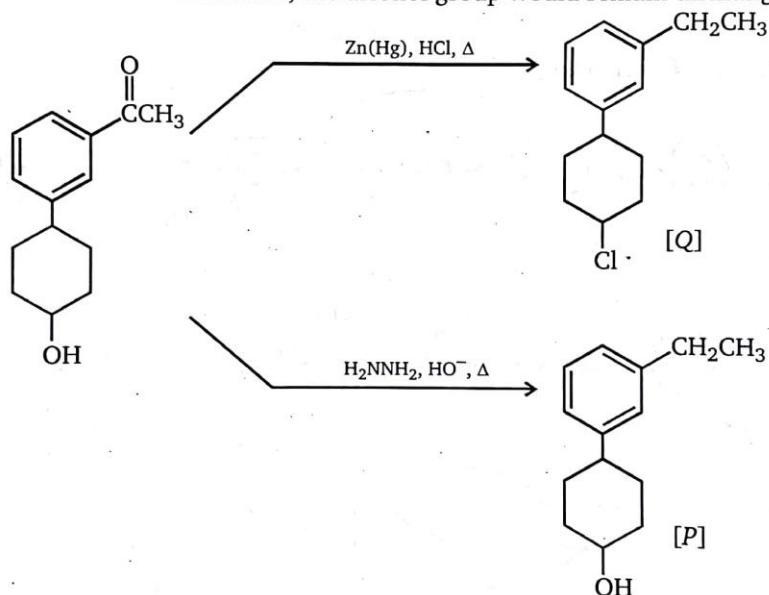
$\xrightarrow{Zn(Hg),\ HCl,\ \Delta}$ benzene ring with CH_2CH_3 and $CH_2CH_2\overset{+}{N}(CH_3)_3\ Cl^-$

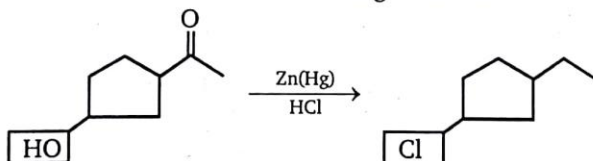
$\xrightarrow{H_2NNH_2,\ HO^-,\ \Delta}$ benzene ring with CH_2CH_3 and $CH{=}CH_2$ $+\ N(CH_3)_3$

3. (d) Wolff-kishner reduction carried out in basic condition clemmensen reduction carried out in acidic condition. Epoxide unstable in acidic and basic medium.

4. (c) Benzene ring with $\overset{O}{\overset{\|}{C}}-CH_3$ and NO_2 $\xrightarrow[HCl]{Zn(Hg)}$ benzene ring with ethyl group and NH_2

5. (a) Wolff-Kishner is favourable because alcohol is stable in basic medium.

6. (c) Heating the following compound with HCl (as required by the Clemmensen reduction) would cause the alcohol to undergo substitution. Under the basic conditions of the Wolff-Kishner reduction, the alcohol group would remain unchanged.

Zn(Hg), HCl, Δ → [Q] (CH_2CH_3 … Cl)

H_2NNH_2, HO^-, Δ → [P] (CH_2CH_3 … OH)

7. (b) In acidic medium alcohol undergo reaction.

HO … Zn(Hg) / HCl → Cl

8. (b) In basic medium halide undergo elimination reaction (E_2 elimination bimolecular).

9. (b) Ether are stable in basic medium.

10. (c) More positive charge of an ketone more will be reactivity toward H_2O.

Hydrates are more stable when electron withdrawing group are attached.

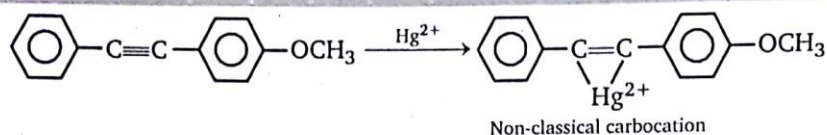
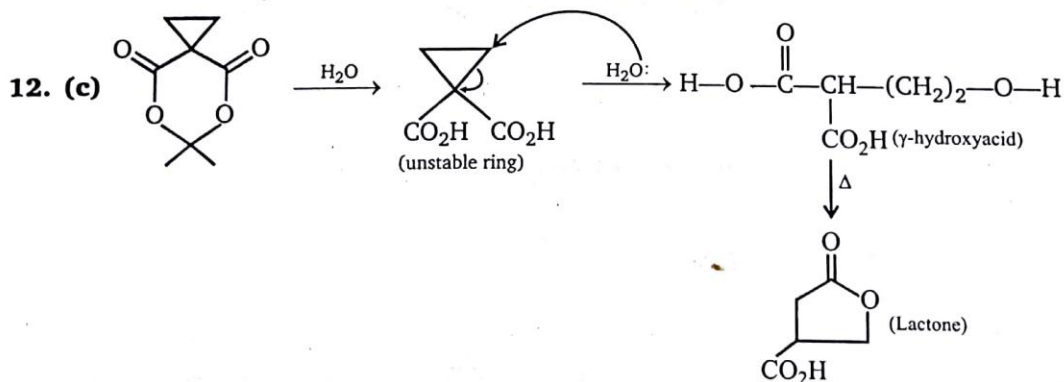
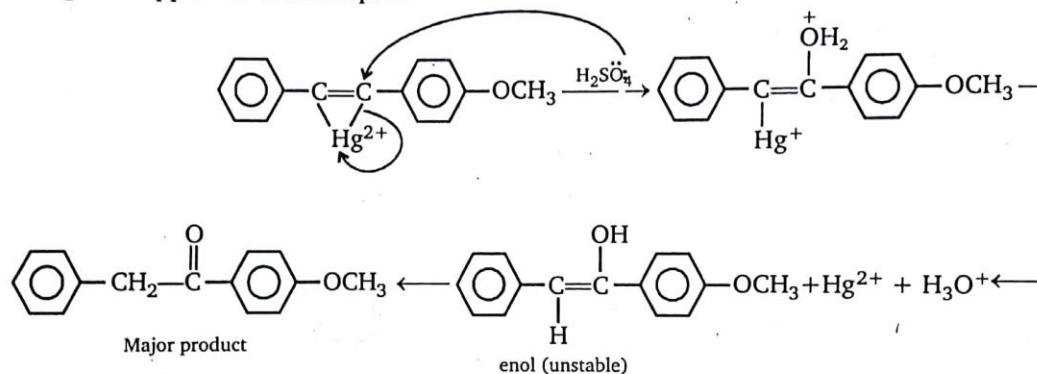
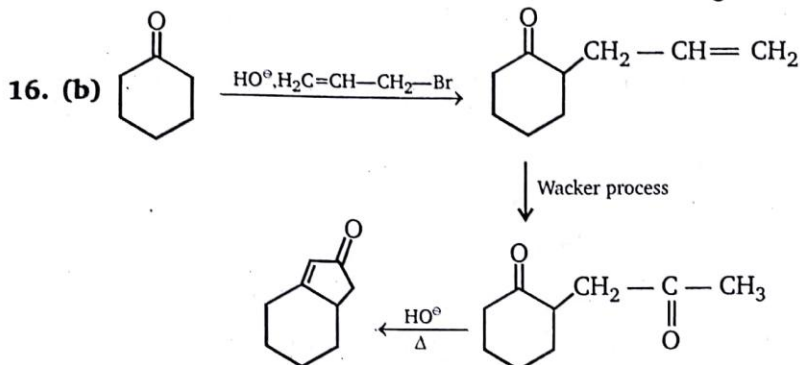
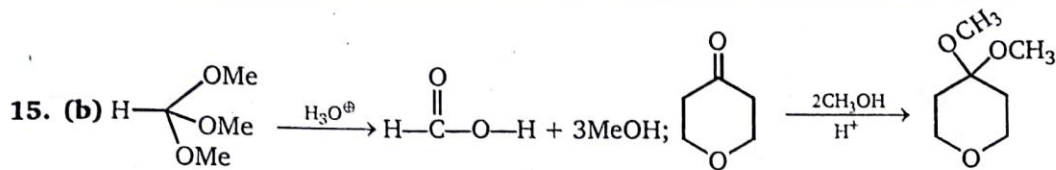
11. (c) Mechanism

Step-I : Approach of electrophile

Fehling is used to differentiate aldehyde and ketone.

15. (b) $H-C(OMe)_3 \xrightarrow{H_3O^{\oplus}} H-\overset{O}{\overset{\|}{C}}-O-H + 3MeOH$; tetrahydropyran-4-one $\xrightarrow[H^+]{2CH_3OH}$ 4,4-dimethoxytetrahydropyran (OCH_3, OCH_3)

16. (b) Cyclohexanone $\xrightarrow{HO^{\ominus}, H_2C=CH-CH_2-Br}$ 2-($CH_2-CH=CH_2$)cyclohexanone

$\downarrow$ Wacker process

2-($CH_2-\underset{\|}{\overset{}{C}}(=O)-CH_3$)cyclohexanone $\xrightarrow[\Delta]{HO^{\ominus}}$ bicyclic enone (fused cyclopentenone)

17. (b) Oxidation of ketone will take place. (Insertion of oxygen take place in between)

18. (b) 2-methoxytetrahydrofuran (OCH_3) Acetal give negative Tollen's test

2-hydroxytetrahydrofuran (unstable) $\xrightarrow{HO^{\ominus}} H-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_2-OH$

Hemiacetal give positive Tollen's test.

19. (b) 2-(hydroxymethyl)cyclohexanol (OH, OH) $\xrightarrow{PCC}$ 2-oxocyclohexanecarbaldehyde (CHO) $\xrightarrow[\text{(aldehyde is more reactive than ketone)}]{HOCH_2CH_2OH,\ H^+}$ 2-(1,3-dioxolan-2-yl)cyclohexanone (CH)

$\downarrow CH_3MgBr \mid H_3O^{\oplus}$

2-hydroxy-2-methylcyclohexanecarbaldehyde (OH, CH_3, CHO) $\xrightarrow{NaBH_4}$ 1-methyl-2-(CH_2OH)cyclohexanol (CH_3, OH, CH_2OH)

20. (d) $CH_3-CH=CH_2$
- $\xrightarrow[H_2O_2,\bar{O}H]{BH_3,THF}$ propan-1-ol (OH) (*P*) $\xrightarrow{PCC}$ propanal (=O)
- $\xrightarrow[NaBH_4]{Hg(OAc)_2,H_2O}$ propan-2-ol (OH) (*R*) $\xrightarrow{PCC}$ acetone (O)

21. (b) Al ⟶ Al^{+3} + $3e^{\ominus}$

$e^{\ominus}$ + cyclopentanone → (ketyl) —Dimerization→ dianion ($O^{\ominus}$ $O^{\ominus}$) —H_2O→ OH OH (Pinacole)

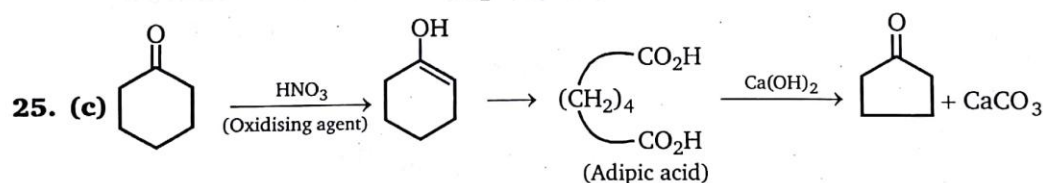
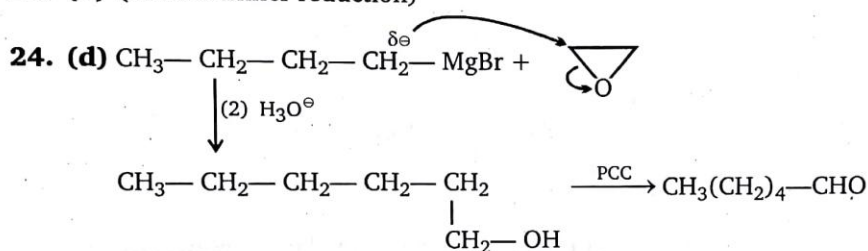
22. (b) More positive charge on carbon and less steric hindrance and unstable reactant will favour nucleophilic attack.

23. (b) (Wolff-Kishner reduction)

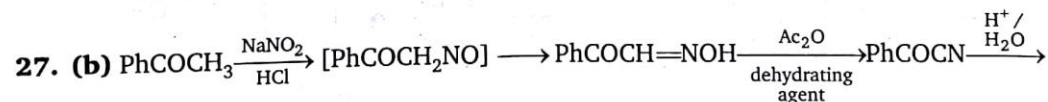
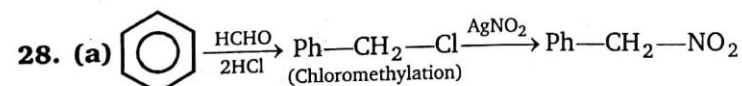
24. (d) $CH_3—CH_2—CH_2—\overset{\delta\ominus}{CH_2}—MgBr$ + ethylene oxide

(2) $H_3O^{\ominus}$

$CH_3—CH_2—CH_2—CH_2—CH_2—CH_2—OH$ $\xrightarrow{PCC}$ $CH_3(CH_2)_4—CHO$

25. (c) Cyclohexanone $\xrightarrow[\text{(Oxidising agent)}]{HNO_3}$ enol (OH) ⟶ $(CH_2)_4(CO_2H)_2$ (Adipic acid) $\xrightarrow{Ca(OH)_2}$ cyclopentanone + $CaCO_3$

26. (b) $Ph—\overset{O}{\overset{||}{C}}—H$, Nucleophilic addition take place and then hemiacetal will form which will undergo nucleophilic attack.

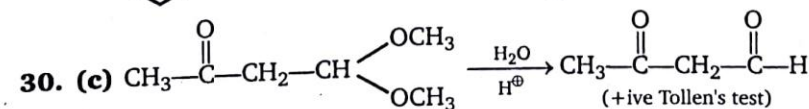
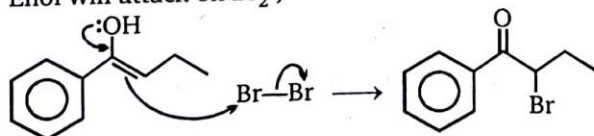
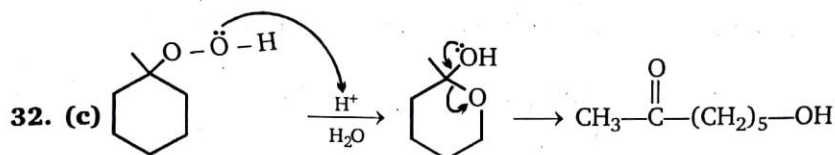
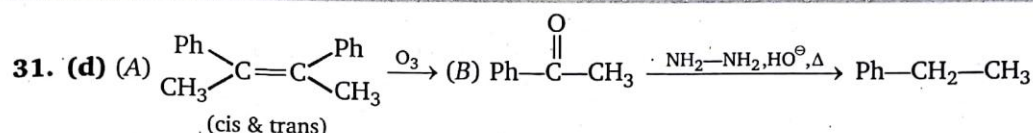
27. (b) $PhCOCH_3 \xrightarrow[HCl]{NaNO_2} [PhCOCH_2NO] \longrightarrow PhCOCH{=}NOH \xrightarrow[\text{dehydrating agent}]{Ac_2O} PhCOCN \xrightarrow{H^+/H_2O}$ $PhCOCO_2H$

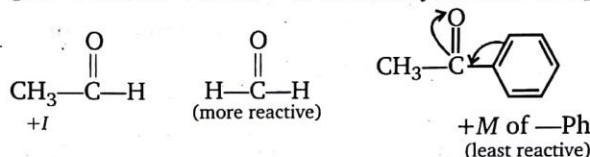
28. (a) Benzene $\xrightarrow[2HCl]{HCHO}$ $Ph—CH_2—Cl$ (Chloromethylation) $\xrightarrow{AgNO_2}$ $Ph—CH_2—NO_2$

29. (b) Enol will attack on Br_2,

Ph–C(:OH)=CH–CH₂CH₃ + Br—Br ⟶ Ph–CO–CH(Br)–CH₂CH₃

30. (c) $CH_3—\overset{O}{\overset{||}{C}}—CH_2—CH(OCH_3)_2 \xrightarrow[H^{\oplus}]{H_2O} CH_3—\overset{O}{\overset{||}{C}}—CH_2—\overset{O}{\overset{||}{C}}—H$ (+ive Tollen's test)

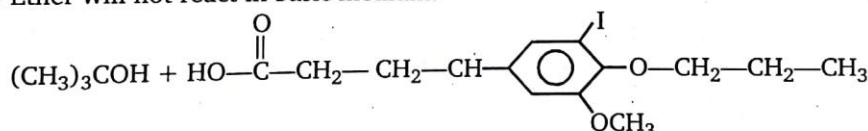
31. (d) (A) $\underset{CH_3}{\overset{Ph}{>}}C=C\underset{CH_3}{\overset{Ph}{<}}$ (cis & trans) $\xrightarrow{O_3}$ (B) $Ph-\overset{O}{\overset{||}{C}}-CH_3 \xrightarrow{NH_2-NH_2, HO^{\ominus}, \Delta} Ph-CH_2-CH_3$

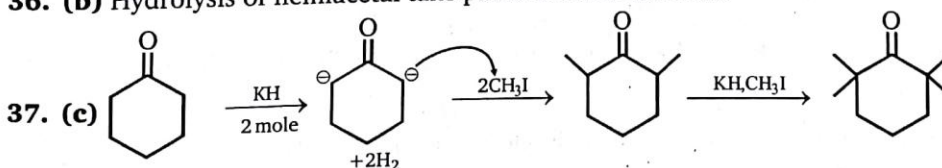
32. (c) (1-methylcyclohexyl hydroperoxide, O–Ö–H) $\xrightarrow[H_2O]{H^+}$ (cyclic intermediate with OH and ring O) $\longrightarrow CH_3-\overset{O}{\overset{||}{C}}-(CH_2)_5-OH$

33. (b) $-CH_3$ group give $+M$ and $+I$ but $+M$ work only at *ortho* and *para* position.

$CH_3-\overset{O}{\overset{||}{C}}-H$ ($+I$) $\quad H-\overset{O}{\overset{||}{C}}-H$ (more reactive) $\quad CH_3-\overset{O}{\overset{||}{C}}-C_6H_5$ ($+M$ of $-Ph$) (least reactive)

Reactivity $\propto$ positive charge on carbonyl carbon so that's why reactivity II > I > III.

34. (b) Nucleophilic addition then hemiacetal will form, which will again undergo nucleophilic attack.

35. (a) Ether will not react in basic medium.

$(CH_3)_3COH + HO-\overset{O}{\overset{||}{C}}-CH_2-CH_2-CH-$ (benzene ring bearing I and OCH_3) $-O-CH_2-CH_2-CH_3$

36. (b) Hydrolysis of hemiacetal take place in acidic medium.

37. (c) Cyclohexanone $\xrightarrow[2\,mole]{KH}$ dianion (both α-carbons $\ominus$) $+2H_2$ $\xrightarrow{2CH_3I}$ 2,6-dimethylcyclohexanone $\xrightarrow{KH, CH_3I}$ 2,2,6,6-tetramethylcyclohexanone

38. (d) Number of carbon decreases.

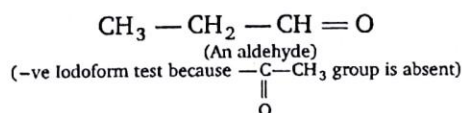
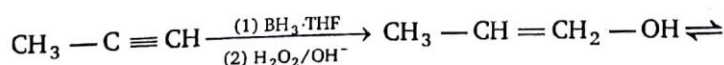
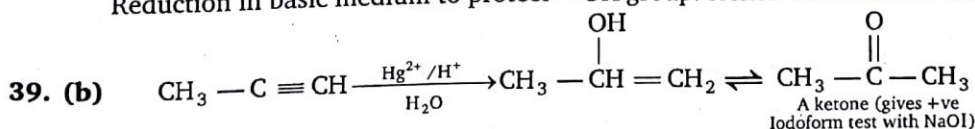
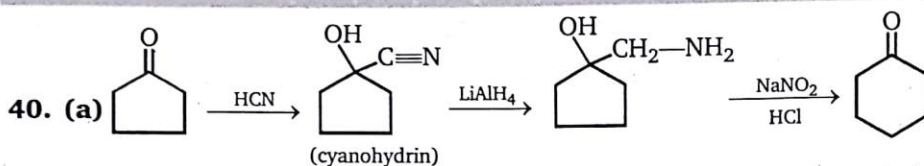
Reduction in basic medium to protect —OH group. Hence wolff-kishner reduction.

39. (b) $CH_3-C\equiv CH \xrightarrow[H_2O]{Hg^{2+}/H^+} CH_3-\overset{OH}{\overset{|}{C}H}=CH_2 \rightleftharpoons CH_3-\overset{O}{\overset{||}{C}}-CH_3$ (A ketone (gives +ve Iodoform test with NaOI))

$CH_3-C\equiv CH \xrightarrow[(2)\ H_2O_2/OH^-]{(1)\ BH_3\cdot THF} CH_3-CH=CH_2-OH \rightleftharpoons$

$CH_3-CH_2-CH=O$ (An aldehyde) (–ve Iodoform test because $-\overset{O}{\overset{||}{C}}-CH_3$ group is absent)

40. (a) Cyclopentanone $\xrightarrow{HCN}$ 1-hydroxycyclopentane-1-carbonitrile (cyanohydrin) $\xrightarrow{LiAlH_4}$ 1-(aminomethyl)cyclopentan-1-ol (OH, $CH_2—NH_2$) $\xrightarrow[HCl]{NaNO_2}$ cyclohexanone

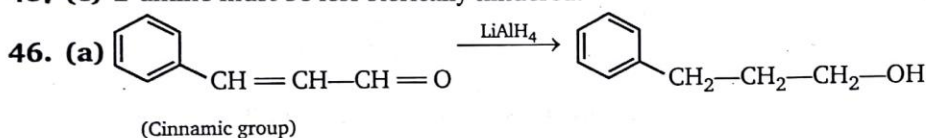
(cyanohydrin)

41. (b) 2, 4-DNP test for aldehyde & ketone. Methyl ketone given positive haloform test.

42. (a) $R—\overset{O}{\overset{\|}{\underset{\delta\oplus}{C}}}—R$ more positive on carbon of carbonyl.

43. (a) Aldehyde is more reactive than ketone toward nucleophilic attack. (Aliphatic aldehyde is more reactive than aromatic aldehyde)

44. (b) Hemiacetal $\longrightarrow$ presence of alcohol and ether on same carbon.

45. (c) 2°amine must be less sterically hindered.

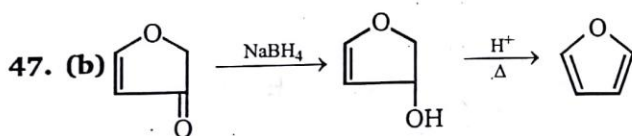
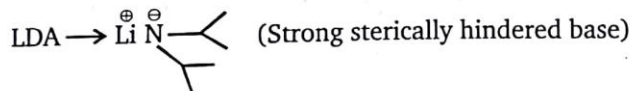
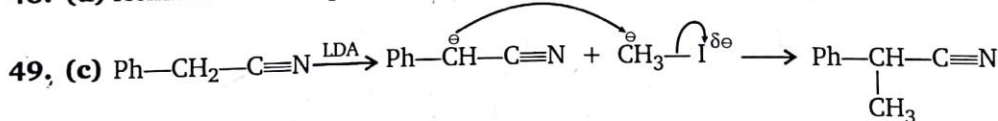
46. (a) $C_6H_5—CH=CH—CH=O \xrightarrow{LiAlH_4} C_6H_5—CH_2—CH_2—CH_2—OH$

(Cinnamic group)

$LiAlH_4$ reduces cinnamic group.

47. (b) Furan-3(2H)-one $\xrightarrow{NaBH_4}$ 2,3-dihydrofuran-3-ol (OH) $\xrightarrow[\Delta]{H^+}$ furan

48. (d) Hemiacetal $\longrightarrow$ presence of alcohol and ether on same carbon.

49. (c) $Ph—CH_2—C\equiv N \xrightarrow{LDA} Ph—\overset{\ominus}{C}H—C\equiv N + \overset{\ominus}{C}H_3—I^{\delta\ominus} \longrightarrow Ph—\underset{CH_3}{\underset{|}{C}H}—C\equiv N$

$LDA \longrightarrow \overset{\oplus}{Li}\,\overset{\ominus}{N}(iPr)_2$ (Strong sterically hindered base)

(Lithium Di-isopropylamide)

50. (b) Iodoform test.

(a) Oxidative ozonolysis by not $KMnO_4$

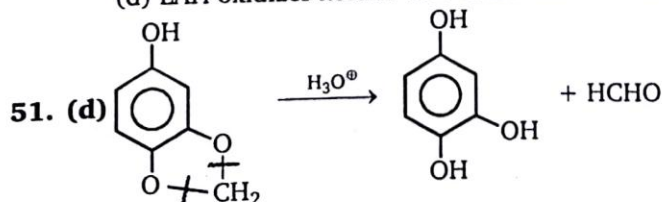
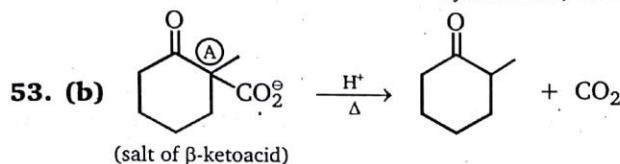
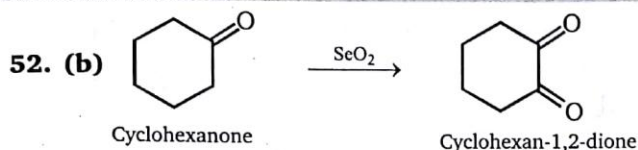
(b) Iodoform test. Only methyl ketones. No reaction with double bond.

(c) H_2/Pt can reduce only double bond.

(d) LAH oxidizes ketone to 2° alcohol not to carboxylic acid.

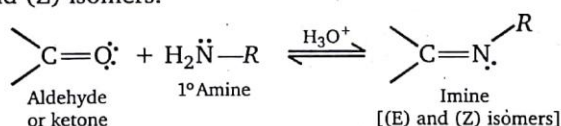
51. (d) 3,4-methylenedioxyphenol (OH; O—CH_2—O bonds cleaved) $\xrightarrow{H_3O^{\oplus}}$ 1,2,4-trihydroxybenzene (OH, OH, OH) + HCHO

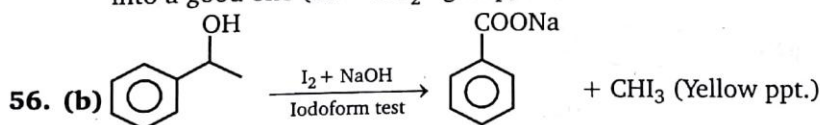
52. (b) Cyclohexanone $\xrightarrow{SeO_2}$ Cyclohexan-1,2-dione

53. (b) (salt of β-ketoacid) $\xrightarrow[\Delta]{H^+}$ 2-methylcyclohexanone + CO_2

54. (c) Hydrolysis of ether.

55. (b) A general equation for the formation of an imine from a primary amine and an aldehyde or ketone is shown here. Imine formation is acid catalyzed, and the product can form as a mixture of (E) and (Z) isomers.

$$>C{=}\ddot{O}: + H_2\ddot{N}{-}R \xrightleftharpoons{H_3O^+} >C{=}\ddot{N}{-}R$$

Aldehyde or ketone; 1° Amine; Imine [(E) and (Z) isomers]

Imine formation generally takes place fastest between pH 4 and 5 and is slow at very low or very high pH. We can understand why an acid catalyst is necessary if we consider the mechanism that has been proposed for imine formation. The important step is the step in which the protonated aminoalcohol loses a molecule of water to become an iminium ion. By protonating the alcohol group, the acid converts a poor leaving group (an – OH group) into a good one (an —OH_2^+ group).

56. (b) $C_6H_5CH(OH)CH_3 \xrightarrow[\text{Iodoform test}]{I_2 + NaOH} C_6H_5COONa$ + CHI_3 (Yellow ppt.)

57. (a) (*A*) $CH_3-CH_2-CH_2-OH$

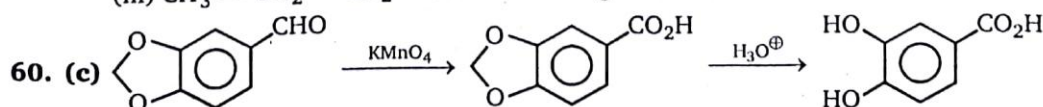
(*B*) CH_3-CH_2-CHO

give positive Tollen's test.

58. (d) Attack at sp^2 carbon take place on above and below the plane of sp^2 carbon.

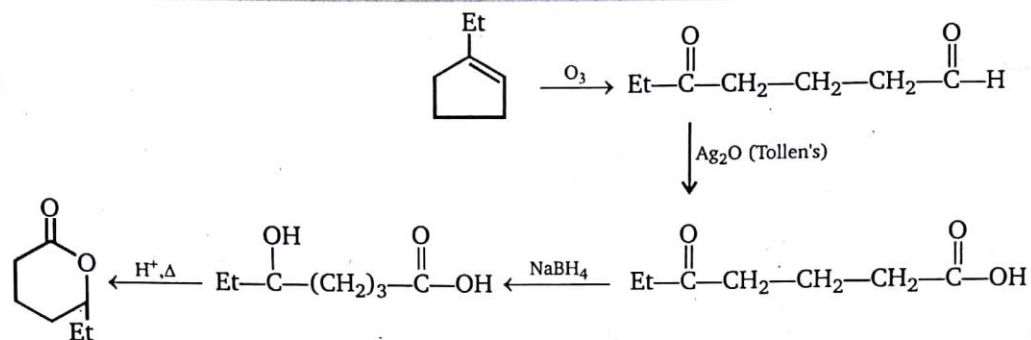
59. (c) (i) CH_3-CH_2-CN (ii) $CH_3-CH_2-CH_2-NH_2$

(iii) $CH_3-CH_2-CH_2-NH-\overset{O}{\overset{\|}{C}}-CH_3$

60. (c) 3,4-methylenedioxybenzaldehyde (CHO) $\xrightarrow{KMnO_4}$ 3,4-methylenedioxybenzoic acid (CO_2H) $\xrightarrow{H_3O^\oplus}$ 3,4-dihydroxybenzoic acid (HO, HO, CO_2H)

61. (c) Wolff-Kishner reduction.

62. (a) (1-ethylcyclopentene) $\xrightarrow{O_3}$ $Et-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-H$

$\downarrow$ Ag_2O (Tollen's)

$Et-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{NaBH_4} Et-\overset{OH}{\overset{|}{C}}-(CH_2)_3-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{H^+,\Delta}$ (lactone, Et)

63. (b) Enolate ion formed in first step.

64. (b) Methyl ketone give positive Tollen's test.

65. (b) (methyl propanoate) $\xrightarrow{\overset{-}{C}H_3\overset{+}{Mg}Br}$ (tetrahedral intermediate with CH_3, $\overset{\ominus}{O}\overset{\oplus}{Mg}Br$) $\rightarrow$ (butanone) + MgBr (OCH_3) $\xrightarrow{CH_3MgBr}$ (2-methylbutan-2-ol, OH)

(3° alc.)

66. (d) $Ph-\overset{O}{\overset{\|}{C}}-CH_3+NH_2OH \longrightarrow \begin{matrix} Ph \\ CH_3 \end{matrix}\!\!>C=N-OH$

(Oxime)

67. (b) $Ca(OH)_2 \xrightarrow[\Delta]{} CaO + H_2O$

$CH_3-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{CaO}$ (calcium acetate: C–C(=O)–O–Ca–O–C(=O)–C)

$\downarrow \Delta(-CaCO_3)$

(acetone)

68. (d) (cyclohexanone) $\underset{H_2O}{\rightleftharpoons}$ (cyclohexane-1,1-diol, OH OH)

(unstable)

69. (b) (c) (b) OH (a) O

70. (b) H H $\xrightarrow[\text{EtOH, }\Delta]{EtO^{\ominus}Na^{\oplus}}$ ⊖ Aromatic stable $CH_3-\overset{O}{\overset{||}{C}}-CH_3$ → OH, $-\underset{CH_3}{C}-CH_3$

Nucleophilic addition take place.

71. (b) $Ph-\overset{O}{\overset{||}{C}}-CH_3 \xrightarrow[H_3O^{\oplus}]{I_2/NaOH} Ph-\overset{O}{\overset{||}{C}}-OH$

(Iodoform)

72. (d) $CH_3-\overset{O}{\overset{||}{C}}-\boxed{CH_2}-C\equiv N$

(acidic)

73. (d) =O $\xrightarrow{H_2NOH/H^{\oplus}}$ =N–OH

(oxime)

74. (a) $Ph-\overset{O}{\overset{||}{C}}-OH \xrightarrow[S_N1]{SOCl_2} Ph-\overset{O}{\overset{||}{C}}-Cl \xrightarrow[\text{Pd-BaSO}_4\text{ Lindlar catalyst}]{H_2} Ph-\overset{O}{\overset{||}{C}}-H$

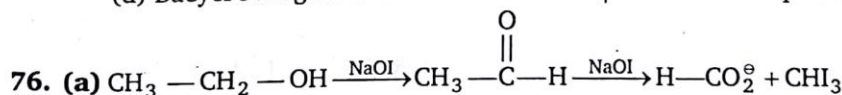
75. (d) Cold dil. alk $KMnO_4$, is Baeyer's reagent.

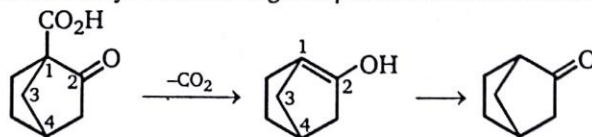
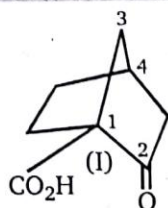
(a) Schiff 's reagent is used to test presence of Aldehydes.

(b) Tollen's reagent is used to test presence of Aldehydes.

(c) Fehling's reagent is used to test presence of Aldehyde.

(d) Baeyer's reagent is cold dil. alk. $KMnO_4$ is used to test presence of unsaturation.

76. (a) $CH_3-CH_2-OH \xrightarrow{NaOI} CH_3-\overset{O}{\overset{||}{C}}-H \xrightarrow{NaOI} H-CO_2^{\ominus} + CHI_3$

77. (a) β-Keto acids undergo decarboxylation through the keto form via a cyclic T. S. which results in the formation of the enol form of the ketone product. The enol then changes to the more stable keto form. If decarboxylation of the given β-keto acid could follow this route, then :

CO_2H, O, 1, 2, 3, 4 $\xrightarrow{-CO_2}$ 1, OH, 2, 3, 4 → O

If we draw the acid as shown in (I), it can be seen that the methylene group forms a bridge, which is perpendicular to the cyclohexane ring.

The enol produced would have a double bond in the 1, 2-position. Thus, C – 1 is sp^2-hybridised and therefore the bond leading to the methylene bridge (1, 3) would have to be coplanar with the groups joined to C – 2 in the enol, *i.e.*, the bridge would have to flatten. This would require the normal valency angles (~ 109.5°) to change to ~ 120°. Even if a compromise situation occurred, *i.e.*, all bond angles involved (∠ s 1, 3, and 4) underwent change, the resulting strain would be very large, too large to be expected for it to occur. Hence, it is reasonable to argue that since decarboxylation does occur, it does so through a route requiring a much higher activation energy than that required for the 'usual' route. Hence the difficulty of decarboxylation. (Bredt's rule)

78. (c) $HOCH_2CH_2CH_2-C(=O)-OCH_2CH_3 \xrightarrow{PCC} H-C(=O)-CH_2CH_2-C(=O)-OCH_2CH_3$

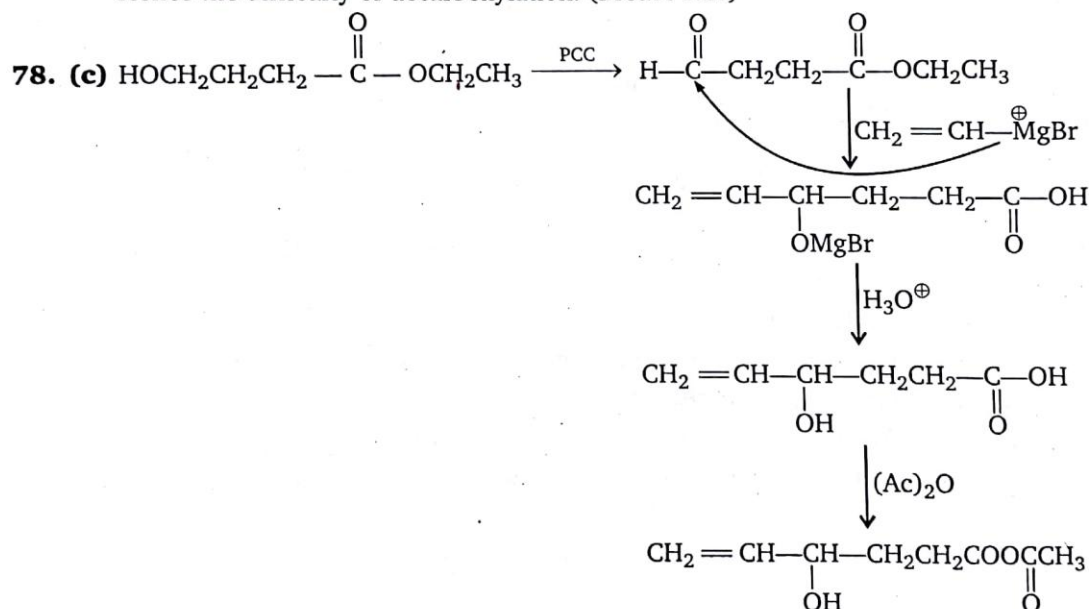
$\downarrow CH_2=CH-\overset{\oplus}{M}gBr$

$CH_2=CH-CH(OMgBr)-CH_2-CH_2-C(=O)-OH$

$\downarrow H_3O^{\oplus}$

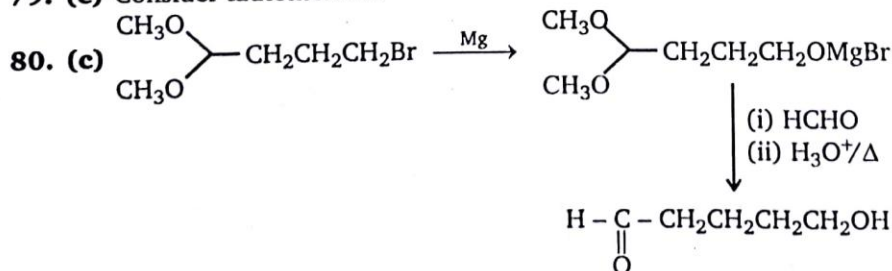
$CH_2=CH-CH(OH)-CH_2CH_2-C(=O)-OH$

$\downarrow (Ac)_2O$

$CH_2=CH-CH(OH)-CH_2CH_2COOC(=O)CH_3$

79. (c) Consider tautomerism.

80. (c) $(CH_3O)_2CH-CH_2CH_2CH_2Br \xrightarrow{Mg} (CH_3O)_2CH-CH_2CH_2CH_2OMgBr$

$\downarrow$ (i) HCHO (ii) H_3O^+/Δ

$H-C(=O)-CH_2CH_2CH_2CH_2OH$

81. (d) Enamine formation.

82. (b) Optically active compound are b & c but only b give negative tollen test.
Ketones give negative Tollen's test and positive 2,4-DNP test.

83. (b) Stork enamine reaction. (most nucleophilic site will attack)

84. (b) PhMgBr ⟶ (cyclopentanone) → (1-phenylcyclopentanol, OH, Ph) → (1-chloro-1-phenylcyclopentane, Ph, Cl) → (1-phenylcyclopentene, Ph).

85. (b) $PhCH_3 \xrightarrow[\text{Etard}]{CrO_2Cl_2} PhCHO \xrightarrow[\text{Cannizaro}]{\text{Conc.KOH}} PhCOO^{\ominus} + PhCH_2OH$

86. (a) CN / H—OH / H—OH / CH_2OH and CN / HO—H / H—OH / CH_2OH (Diastereomers)

87. (b) (cyclopentanone) $\xrightarrow{NH_2OH}$ (oxime, N—OH) (Beckmann rearrengement) $\xrightarrow{H^+}$ (lactam, NH) amide $\xrightarrow{LAH}$ (piperidine, N–H) amine

88. (c) (A) cyclopentyl—$\overset{14}{C}(=O)$—CH_3,

(B) cyclopentyl—$\overset{14}{C}(=O)$—$O^{\ominus}$

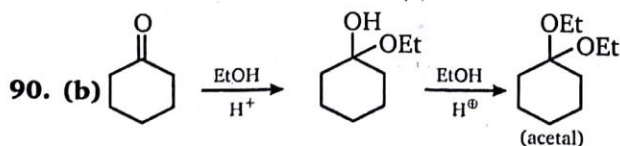
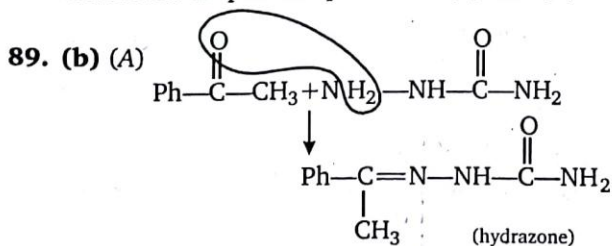
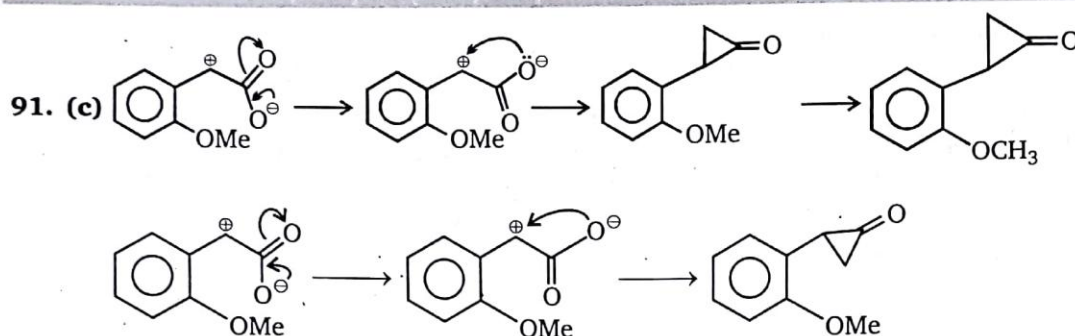
(C) CHI_3

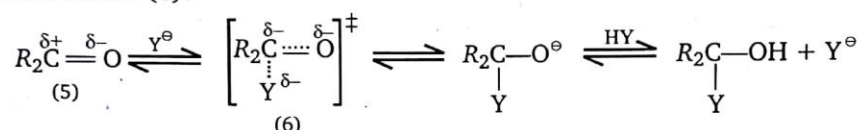
Correction in question product is (A) and (C).

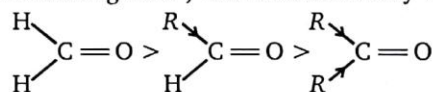
89. (b) (A)
$Ph—C(=O)—CH_3 + NH_2—NH—C(=O)—NH_2$
↓
$Ph—C(CH_3)=N—NH—C(=O)—NH_2$ (hydrazone)

90. (b) (cyclohexanone) $\xrightarrow[H^+]{EtOH}$ (1-ethoxycyclohexanol, OH, OEt) $\xrightarrow[H^{\oplus}]{EtOH}$ (1,1-diethoxycyclohexane, OEt, OEt) (acetal)

91. (c) OMe → OMe → OMe → OCH_3

OMe → OMe → OMe

92. (b) In simple nucleophilic additions where the rate-limiting step is attack by $Y^{\ominus}$, the positive character of the carbonyl carbon atom is reduced on going from the starting material (5) to the transition state (6):

$$\underset{(5)}{R_2\overset{\delta+}{C}=\overset{\delta-}{O}} \underset{}{\overset{Y^{\ominus}}{\rightleftharpoons}} \underset{(6)}{\left[R_2\overset{\delta-}{C}\cdots\overset{\delta-}{O}\ ;\ Y^{\delta-}\right]^{\ddagger}} \rightleftharpoons R_2C(Y)-O^{\ominus} \overset{HY}{\rightleftharpoons} R_2C(Y)-OH + Y^{\ominus}$$

We should thus expect the rate of addition to be reduced by electron-donating *R* groups and enhanced by electron-withdrawing ones ; this is borne out by the observed sequence :

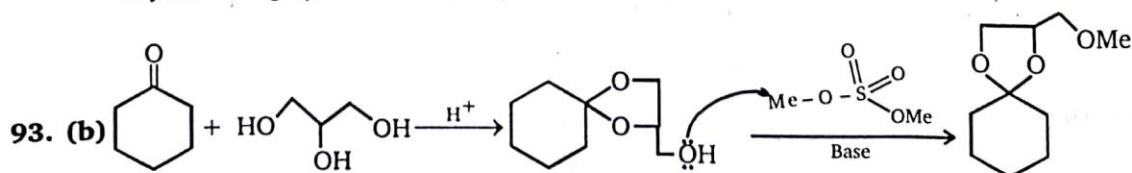
$$H_2C=O > RHC=O > R_2C=O$$

In the above examples steric, as well as electronic, effect could be influencing relative rates of reaction, but the influence of electronic effects alone may be seen in the series of compounds (11) :

So far as steric effects are concerned, the least energy - demanding direction of approach by the nucleophile to the carbonyl carbon atom will be from above, or below, the substantially planar carbonyl compound. It is also likely to be from slightly to the rear of the carbon atom, because of potential coulombic repulsion between the approaching nucleophile and the high electron density at the carbonyl oxygen atom :

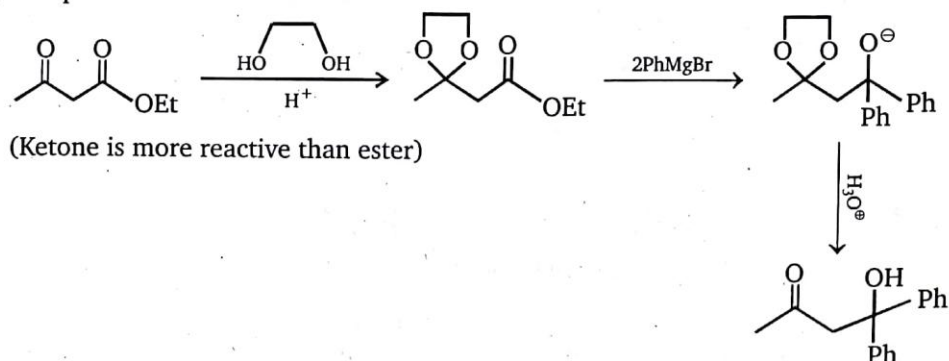
Thus the Ks for cyanohydrin formation are found to reflect this operation of both steric and electronic factors:

	K
CH_3CHO	very large
C_6H_5CHO	210
$CH_3COCH_2CH_3$	38
$C_6H_5COCH_3$	0.8

Highly hindered ketones, such as $Me_3CCOCMe_3$, may not react at all except possibly with very small, highly reactive nucleophilies.

93. (b) (cyclohexanone) + HO–CH₂–CH(OH)–CH₂–OH $\xrightarrow{H^+}$ (spiro dioxolane)–CH₂–ÖH $\xrightarrow[\text{Base}]{Me-O-SO_2-OMe}$ (spiro dioxolane)–CH₂–OMe

94. (b) End product of the reaction is

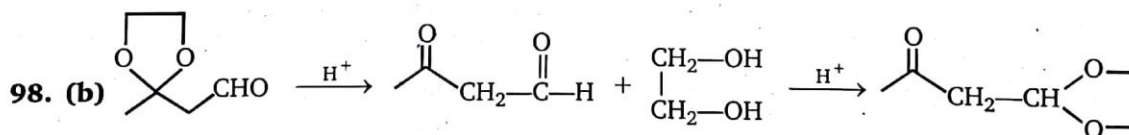
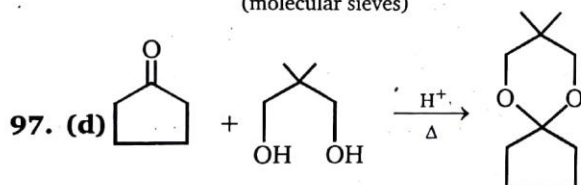
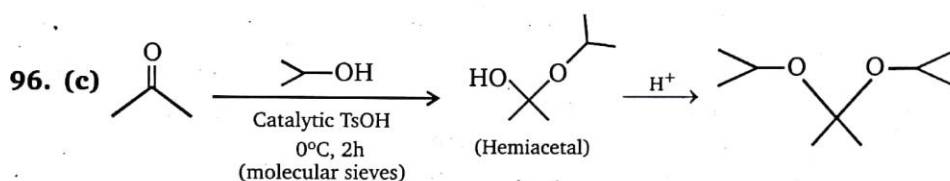
HO⌒OH, H^+ → ; 2PhMgBr → ; $H_3O^{\oplus}$ ↓

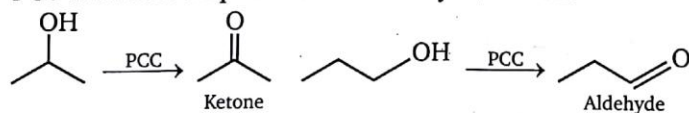
(Ketone is more reactive than ester)

95. (c) Ph—CH = CH—C≡C—CHO → does not undergo self aldol condensation

O_3 → Ph—CHO + 2B $\xrightarrow{Ag^+}$ oxalic acid

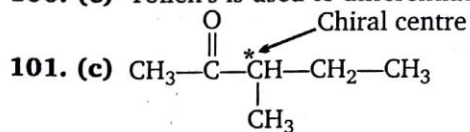
96. (c) —OH, Catalytic TsOH, 0°C, 2h (molecular sieves) → (Hemiacetal) $\xrightarrow{H^+}$

97. (d) + OH OH $\xrightarrow[\Delta]{H^+}$

98. (b) CHO $\xrightarrow{H^+}$ CH_2—C(=O)—H + CH_2—OH / CH_2—OH $\xrightarrow{H^+}$ CH_2—CH

99. (c) PCC is used to stop reaction at Aldehyde/Ketone.

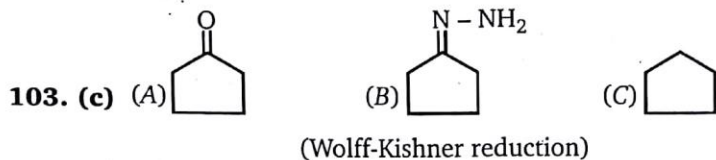
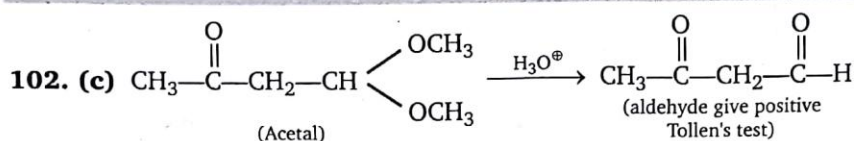
OH $\xrightarrow{PCC}$ Ketone; OH $\xrightarrow{PCC}$ Aldehyde

Tollen's reagent is used to differentiate aldehydes from ketones.

100. (c) Tollen's is used to differentiated aldehyde and ketone.

101. (c) CH_3—C(=O)—$\overset{*}{C}H$(CH_3)—CH_2—CH_3 (Chiral centre)

2,4-DNP is test for aldehyde and ketone

102. (c) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH(OCH_3)_2$ (Acetal) $\xrightarrow{H_3O^{\oplus}}$ $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-H$ (aldehyde give positive Tollen's test)

103. (c) (A) cyclopentanone (B) cyclopentanone hydrazone ($N-NH_2$) (C) cyclopentane

(Wolff-Kishner reduction)

104. (c) $NaHSO_3$ will react with aldehyde and methyl ketone only.

105. (c) 2-($CH_2-CH_2-CH_2-NH_2$)cyclohexanone $\xrightarrow{\Delta}$ (cyclic imine) $+H_2O$ $\xrightarrow{H_2/Ni}$ (decahydroquinoline, N–H)

106. (b) cyclohexane-1,3-dione $\xrightarrow[\text{(acid–base)}]{KOH}$ (enolate, $\ominus$ at C-2) $\xrightarrow{H_2C=CH-CH_2-Br}$ 2-($CH_2-CH=CH_2$)cyclohexane-1,3-dione

107. (d) (cyclohexylidene)–COOH $\xrightarrow{CH_3Li}$ (cyclohexylidene)–$COCH_3$ $\xrightarrow[NaOH]{I_2}$ (cyclohexenyl)–COONa

108. (c) cyclopentanone $\xrightarrow[D_2O]{KOD}$ 2,2,5,5-tetradeuteriocyclopentanone $\xrightarrow{LiAlH_4}$ 2,2,5,5-tetradeuteriocyclopentanol (OH) $\xrightarrow{H^+,\Delta}$ D,D / D cyclopentene

109. (c) (A) $CH_3-\underset{}{\overset{OH}{\overset{|}{CH}}}-CN$ (B) $CH_3-\overset{OH}{\overset{|}{CH}}-CO_2H$ (C) $CH_3-CH\langle$ O–C(=O) / C(=O)–O $\rangle CH-CH_3$ (Lactide)

(D) $CH_3-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH_2}}$ (E) $CH_3-\overset{O}{\overset{\|}{C}}-H+HCHO$

110. (b) Aldehyde is more reactive than ketone, $-I$ effect increases reactivity toward nucleophilic attack.

111. (c) 2-acetylcyclohexanone ($\overset{O}{\overset{\|}{C}}-CH_3$) $\xrightarrow[(2)H^+]{(i)\ I_2+NaOH}$ 2-oxocyclohexane–CO_2H $\xrightarrow{\Delta}$ cyclohexanone $+ CO_2$

112. (b) $Ph{-}CH_2{-}CN \xrightarrow{EtO^{\ominus}Na^{\oplus}} Ph{-}\overset{\ominus}{C}H{-}CN + CH_3{-}\overset{O}{\overset{\|}{C}}{-}Cl \longrightarrow Ph{-}\underset{CN}{\underset{|}{C}H}{-}\overset{O}{\overset{\|}{C}}{-}CH_3 \xrightarrow{H_3O^{\oplus}} Ph{-}\underset{CO_2H}{\underset{|}{\overset{\alpha}{C}H}}{-}\overset{O}{\overset{\|}{\underset{\beta}{C}}}{-}CH_3$ (β-ketoacid) $\xrightarrow{\Delta} Ph{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}CH_3 + CO_2$

113. (b) (Chiral centre) CHO $\xrightarrow{NaCN}$ CH(OH)—CN + CH(CN)—OH

Diastereomers

114. (c) $CH_3{-}C\equiv C{-}CH_3 \xrightarrow[H_2SO_4]{HgSO_4}$ butan-2-one $\xrightarrow{LiAlH_4}$ butan-2-ol (racemic)

115. (c) $CH_3{-}CH{=}\overset{:OH}{\overset{|}{C}}{-}CH_3\overset{\oplus}{N}{=}O \rightleftharpoons CH_3{-}\underset{N=O}{\underset{|}{C}H}{-}\overset{O}{\overset{\|}{C}}{-}CH_3 \rightleftharpoons CH_3{-}\underset{N{-}O{-}H}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}CH_3$

116. (a)

1-Indanone $\xrightarrow{NH_2OH}$ oxime (N—OH) + oxime (HO—N)

(Beckmann rearrangement) $H^{\oplus}$ → (amide) $\xrightarrow{LiAlH_4}$ (amine)

$H^{\oplus}$ → lactam (N—H) $\xrightarrow{LiAlH_4}$ amine (N—H)

117. (b) (A) $CH{=}CH{-}NO_2$ (methylenedioxy, O / O) (by nitro aldol) $\xrightarrow{HCl}$ HO, OH, $CH{=}CH{-}NO_2$

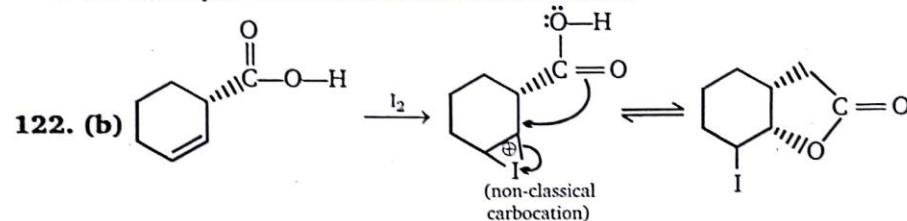
118. (a)

HCN → LiAlH$_4$ → NaNO$_2$ / H$^+$

119. (b) Cl ... Cl $\xrightarrow{\overset{\ominus}{K}OH}$ ... $\xrightarrow{N.G.P.}$

120. (c) Base stronger than cyanide is used as a catalyst.

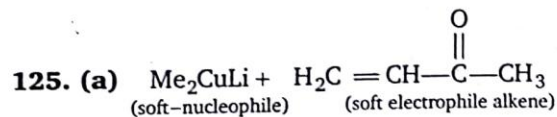
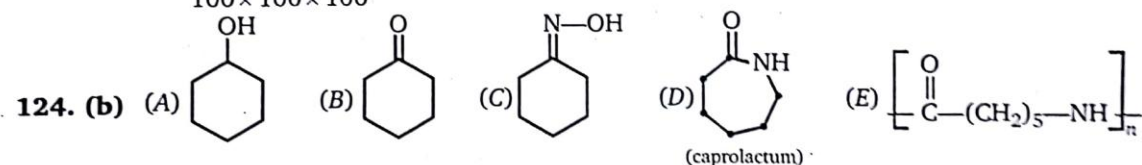
121. (b) Aldehyde will be more reactive than ketone.

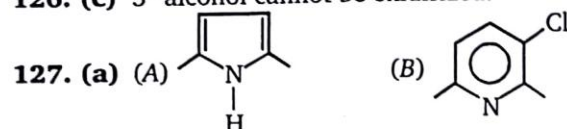
122. (b) $\xrightarrow{I_2}$ (non-classical carbocation) ⇌

123. A – c ; B – b

(A) $\dfrac{58 \times 54 \times 68}{100 \times 100 \times 100} = 21.29$

124. (b) (*A*) (*B*) (*C*) (*D*) (caprolactum) (*E*) $\left[-\overset{O}{\overset{\|}{C}}-(CH_2)_5-NH- \right]_n$

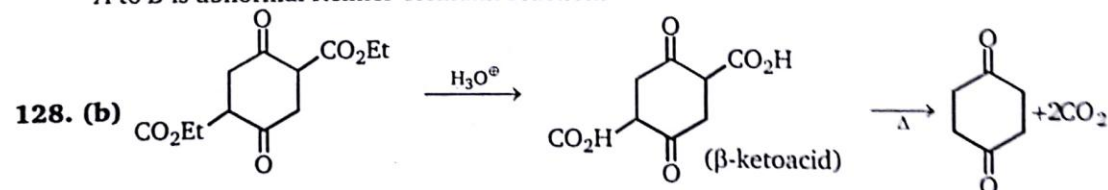
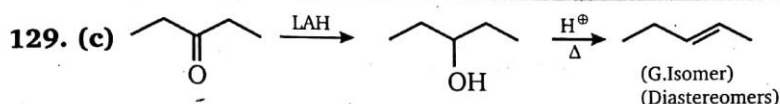
125. (a) $Me_2CuLi + H_2C=CH-\overset{O}{\overset{\|}{C}}-CH_3$

(soft–nucleophile) (soft electrophile alkene)

126. (c) 3° alcohol cannot be oxidisized.

127. (a) (*A*) (*B*)

A to *B* is abnormal Reimer Tiemann reaction.

128. (b) $\xrightarrow{H_3O^{\oplus}}$ (β-ketoacid) $\xrightarrow{\Delta}$ $+ 2CO_2$

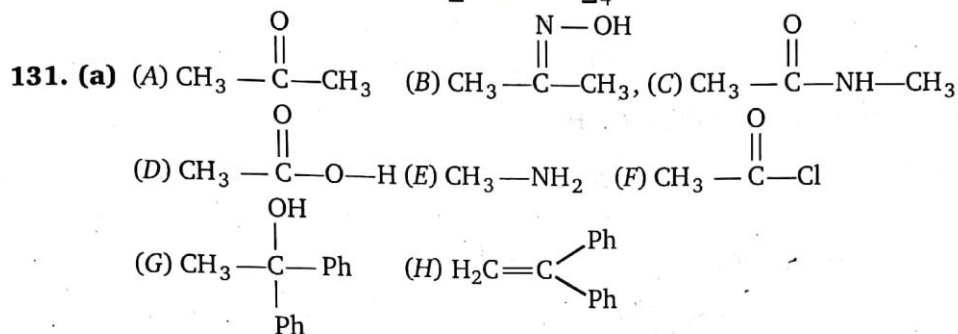
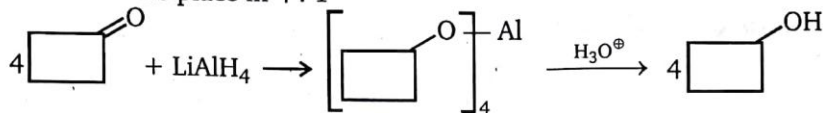
129. (c) 3-pentanone $\xrightarrow{LAH}$ 3-pentanol (OH) $\xrightarrow[\Delta]{H^{\oplus}}$ 2-pentene

(G.Isomer)
(Diastereomers)

130. (a) Reaction take place in 4 : 1

$$4\,\text{(cyclobutanone)} + LiAlH_4 \longrightarrow [\text{(cyclobutyl–O)}]_4Al \xrightarrow{H_3O^{\oplus}} 4\,\text{(cyclobutanol, OH)}$$

131. (a) (*A*) $CH_3-\overset{O}{\overset{||}{C}}-CH_3$ (*B*) $CH_3-\overset{N-OH}{\overset{||}{C}}-CH_3$, (*C*) $CH_3-\overset{O}{\overset{||}{C}}-NH-CH_3$

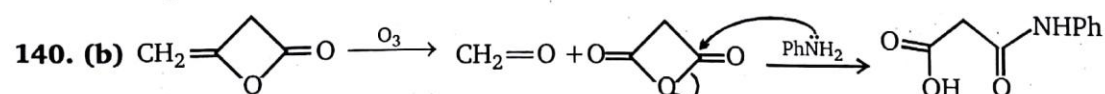
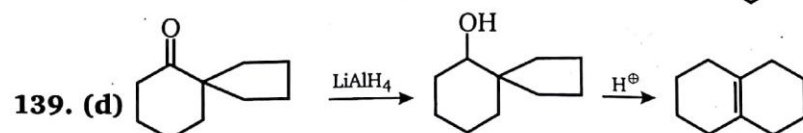
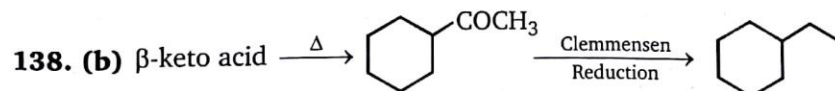
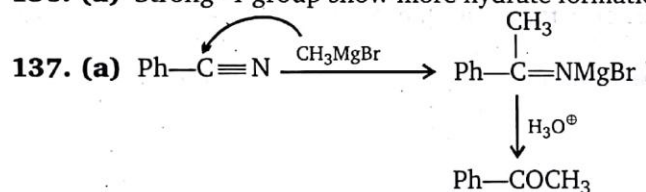
(*D*) $CH_3-\overset{O}{\overset{||}{C}}-O-H$ (*E*) CH_3-NH_2 (*F*) $CH_3-\overset{O}{\overset{||}{C}}-Cl$

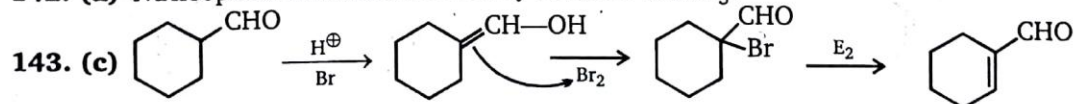
(*G*) $CH_3-C(OH)(Ph)-Ph$ (*H*) $H_2C=C(Ph)_2$

132. (c) Geminal diol will be formed.
133. (d) Informative question.
134. (a) Hydrate formation take place at less than pK_a value.
135. (a) Releif angle strain.
136. (a) Strong –*I* group show more hydrate formation.

137. (a) $Ph-C\equiv N \xrightarrow{CH_3MgBr} Ph-\overset{CH_3}{\overset{|}{C}}=NMgBr \xrightarrow{H_3O^{\oplus}} Ph-COCH_3$

138. (b) β-keto acid $\xrightarrow{\Delta}$ cyclohexyl–$COCH_3$ $\xrightarrow{\text{Clemmensen Reduction}}$ ethylcyclohexane

139. (d) spiro ketone (O) $\xrightarrow{LiAlH_4}$ spiro alcohol (OH) $\xrightarrow{H^{\oplus}}$ octahydronaphthalene

140. (b) $CH_2=$(ring–O)$=O \xrightarrow{O_3} CH_2=O + O=$(ring–O)$=O \xrightarrow{PhNH_2}$ $O=C(OH)-CH_2-C(=O)-NHPh$

141. (d) Ozonolysis, aldol, haloform reaction simultaneously.
142. (a) Nucleophilic addition followed by reaction with O_3.

143. (c) cyclohexyl–CHO $\xrightarrow[Br]{H^{\oplus}}$ cyclohexylidene=CH—OH $\xrightarrow{Br_2}$ 1-bromo-cyclohexane-1-CHO $\xrightarrow{E_2}$ cyclohex-1-ene-1-CHO

144. (b) Nucleophilic addition.

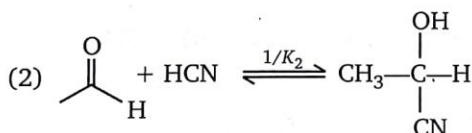
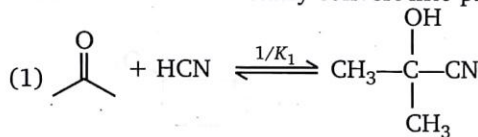
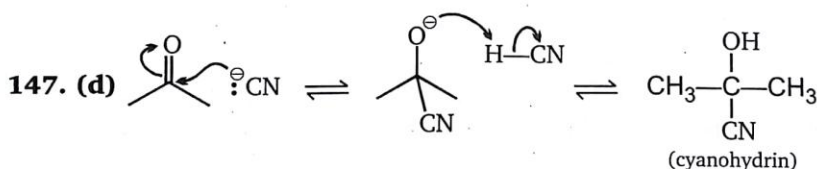
145. (d) $+M$ group decrease the electrophilicity of carbonyl carbon.

146. (b) More steric reactant easily convert into product.

(1) $CH_3COCH_3 + HCN \underset{}{\overset{1/K_1}{\rightleftharpoons}} CH_3-C(OH)(CH_3)-CN$

(2) $CH_3CHO + HCN \underset{}{\overset{1/K_2}{\rightleftharpoons}} CH_3-C(OH)(H)-CN$

$1/K_2 > 1/K_1 \Rightarrow K_1 > K_2$

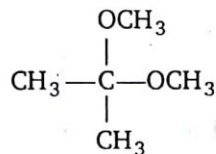
147. (d) $CH_3COCH_3 + {}^{\ominus}CN \rightleftharpoons (CH_3)_2C(O^{\ominus})CN \xrightarrow{H-CN} \rightleftharpoons CH_3-C(OH)(CN)-CH_3$ (cyanohydrin)

No partial positive charge developed on carbon in alkene. Nucleophile ($-C\equiv N$) is added to carbonyl carbon only.

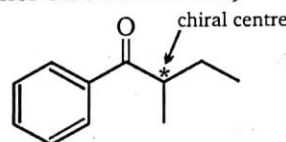
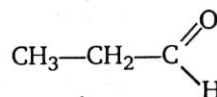
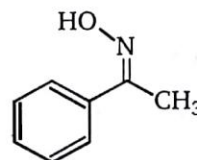
148. (d) Acetal = presence of 2-ether on same carbon.

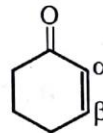
Level-2

1. General Matching Problem

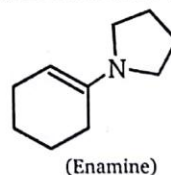
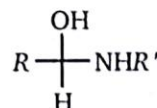
In the box following each description enter a letter designating the best example from the selections at the bottom of the page.

(A) An acetal derivative of a ketone — $CH_3-C(OCH_3)_2-CH_3$

(two ether on same carbon)

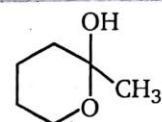
(B) A chiral ketone. — chiral centre

(C) An aldehyde that gives a aldol condensation with itself. — CH_3-CH_2-CHO

(D) An oxime derivative — HO–N=C(CH_3)–Ph

(E) A reagent that reduces aldehydes to 1°- alcohols. — $NaBH_4$ aq. alcohol (reducing agent)

(F) An α, β-unsaturated ketone. — α, β

(G) A reagent that oxidizes aldehydes to carboxylic acids. — $Ag(NH_3)_2^{(+)}\ OH^{(-)}$ (Tollen's reagent)

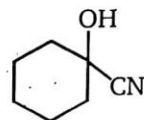
(H) A reagent that reduces ketones to alkanes. — $Zn(Hg)H_3O^{(+)}$ (Clemmensen reduction)

(I) An enamine derivative of a ketone. — N (Enamine)

(J) An intermediate in imine formation. — $R-CH(OH)-NHR'$

(Schiff base) imine

(K) A cyclic hemiacetal.

OH, CH_3, O

Hemiacetal (ether and alcohol on same carbon)

(L) A cyanohydrin derivative. .

OH, CN

(alcohol and cyanide on same carbon)

Answers : (A) l (B) g (C) n (D) k (E) h (F) c (G) j (H) f (I) m (J) d (K) e (L) b

2. (i) $NaBH_4$ will reduce aldehyde ketone and acid chloride

(ii) Ester will undergo hydrolysis in acidic medium.

(iii) Aldehyde and alcohol will be to undergo oxidation.

3. (a) OH (racemic) (Nu-addition reaction)

(b) OH, CN (Nu-addition)

(c) Ph—CH_2—CN (Nu-substitution reaction)

(d) CH, CH_3 (racemic) (Nu-addition reaction)

4. **A** : Ph—CH(OH)—CH_3; **B** : Ph—CH_2—COOH; ; **C** : Ph—CH=C(CH_3)$_2$

D : O, CH_3 ; **E** : CH_2—C(=O)—CH_3, CH_2—C(=O)—CH_3

5. A – c ; B – b

6. (*A*) Ph—CH=CH—CO_2H

(Perkin condensation)

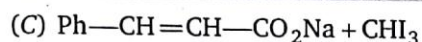
DBE = Double bond equivalent

$$DBE = (C+1) - (\frac{H+X-N}{2})$$

DBE = 6

(*B*) Ph—CH=CH—CH(OH)—CH_3

(Mearwein - Pandorf-verley reduction)

DBE = 5

(C) Ph—CH=CH—$CO_2Na + CHI_3$ DBE = 6

(Iodoform test)

Sum $A + B + C = 17$

7. $+M, +H, +I \propto \dfrac{1}{\text{Nucleophilic attack}}$ $-M, -H, -I \propto$ Nucleophilic attack

Set – (1) (A) – *I* effect of (–Br)

Set – (2) (A) – *I* effect of —C(=O)—

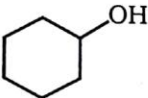
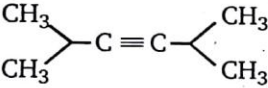
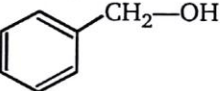
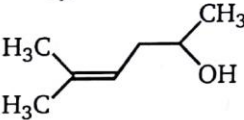
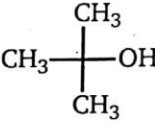
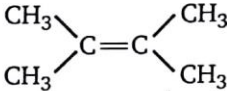
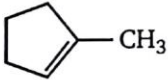
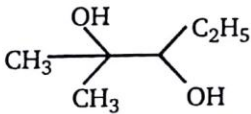
Set – (3) (B) –*M* effect of —NO_2

Set – (4) (B) +*M* effect of phenyl

Set – (5) (A) unstable 3-member ring

Set – (6) (B) +*M* of nitrogen in (A) decreases reactivity

Set – (7) (B) –*M* effect of —C(=O)—O

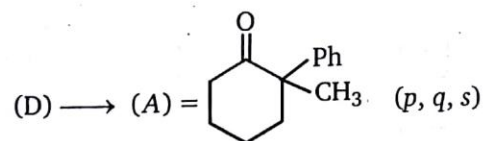
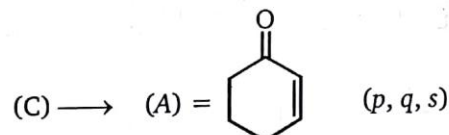
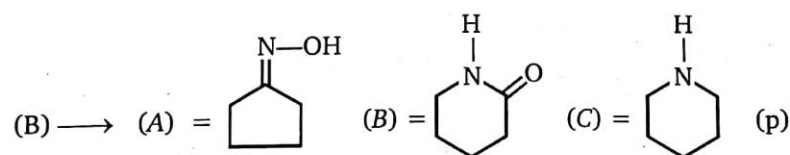
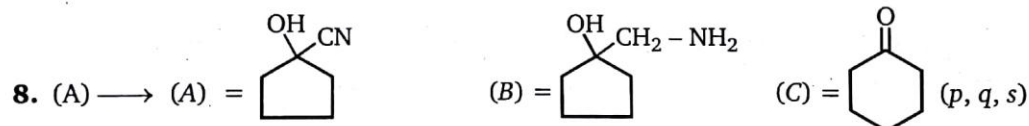
Set – (8) (B) – *I* effect of Cl

Set – (9) (A) +*M* effect of —Ph

Set – (10) (B) (aldehyde > ketone)

8. (A) ⟶ (*A*) = OH, CN (*B*) = OH, $CH_2 - NH_2$ (*C*) = O (*p*, *q*, *s*)

(B) ⟶ (*A*) = N—OH (*B*) = H, N, O (*C*) = H, N (p)

(C) ⟶ (*A*) = O (*p*, *q*, *s*)

(D) ⟶ (*A*) = O, Ph, CH_3 (*p*, *q*, *s*)

9. A : both are oxidized ; B : C^{12} is reduced , C^{14} is oxidized ; C : reduced ; D : oxidized
E : C^{12} is reduced, C^{14} is oxidized ; F : C^{12} is reduced, C^{14} is oxidized

Solution Advanced Problems in Organic Chemistry Part 2 upto Page 240 Aldol and Cannizaro Reactions by M S Chouhan Vibrant Academy Kota for IIT JEE Main Advanced Chemistry Olympiad

10. Formation of Aldehydes and Ketones

Starting	PCC $C_5H_5NHCrO_3Cl$	Jones' Reagent CrO_3 in aq. acid	$Pb(OAc)_4$ [or HIO_4]	(i) O_3 (ii) Zn dust	H_3O^+ & $HgSO_4$	(i) BH_3 in THF (ii) H_2O_2 + NaOH
Cyclohexanol	✓	✓	×	×	×	×
$(CH_3)_2CH-C\equiv C-CH(CH_3)_2$	×	×	×	✓	✓	✓
$C_6H_5-CH_2-OH$	✓	✓	×	✓	×	×
Benzene	×	×	×	✓	×	×
$(H_3C)_2C=CH-CH_2-CH(OH)CH_3$	✓	✓	×	✓	✓	✓
$(CH_3)_3C-OH$	×	×	×	×	×	×
$(CH_3)_2C=C(CH_3)_2$	×	×	×	✓	✓	✓
1-Methylcyclopentene ($-CH_3$)	×	×	×	✓	✓	×
$HO-CH_2CH_2CH_2CH_2-OH$	✓	✓	×	×	×	×
$CH_3-C(OH)(CH_3)-CH(OH)-C_2H_5$	✓	✓	✓	×	×	×

11. A – a ; B – a; C – b ; D – b ; E – a ; F – b

(B)

(a) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_2-\underset{H}{\underset{|}{C}H}-\overset{\oplus}{P}Ph_3 \xrightarrow{\overset{\delta-}{Ph}-\overset{\delta+}{Li}} CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_2-\overset{\ominus}{C}H-\overset{\oplus}{P}Ph_3$

$\rightarrow$ cyclic intermediate ($O^{\ominus}$ on CH_3-C, $CH-\overset{\oplus}{P}Ph_3$; ring H_2C, CH_2-CH_2) $\rightarrow$ 1-methylcyclopentene + PPh_3O

(C) PPh_3 and O should be on same side.
Hence trans-2-butene will be formed.

(D)

(b) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{C}H}-\overset{O}{\overset{\|}{P}}-(OEt)_2 \xrightarrow{\overset{\ominus}{NaH}}$

$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{C}H-\overset{O}{\overset{\|}{P}}-(OEt)_2$

$\downarrow$

cyclic intermediate ($CH_3-C(O^{\ominus})-HC(P(=O)(OEt_2))$; ring CH_2, $CH_2-C(=O)$, CH_2) $\rightarrow$ 3-methylcyclohex-2-en-1-one

(F)

(a) CH_2-Br, CH_2-Br $\xrightarrow{2\ddot{P}Ph_3}$ $CH_2-\overset{\oplus}{P}Ph_3$, $CH_2-\overset{\oplus}{P}Ph_3$ $\xrightarrow{2\overset{\ominus}{Ph}\overset{\oplus}{Li}}$ $\overset{\ominus}{C}H-\overset{\oplus}{P}Ph_3$, $\overset{\ominus}{C}H-\overset{\oplus}{P}Ph_3$

CHO–CHO

$\overset{\oplus}{P}Ph_3$, $\overset{\ominus}{O}$, CH, CH, C–H, H–C, $\oplus PPh_3$, $O^{\ominus}$ ⟶ naphthalene

12. a – q ; b – s; c – r; d – p

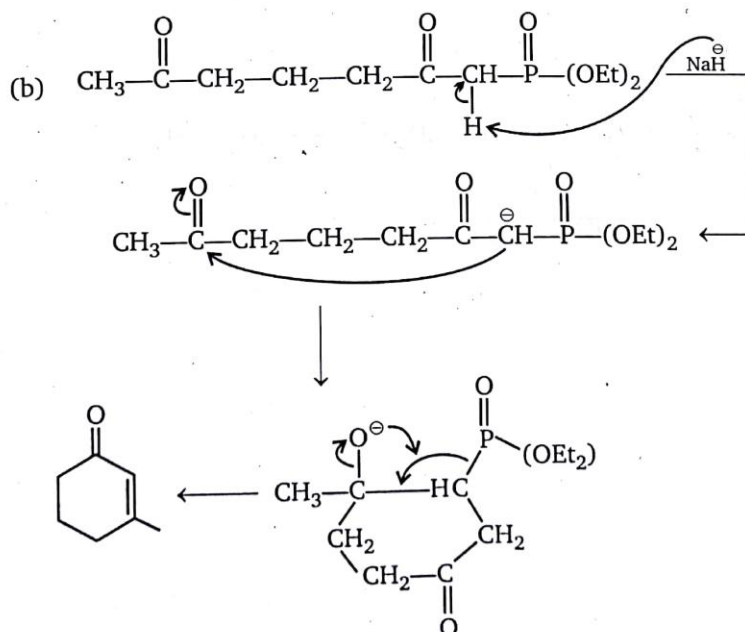
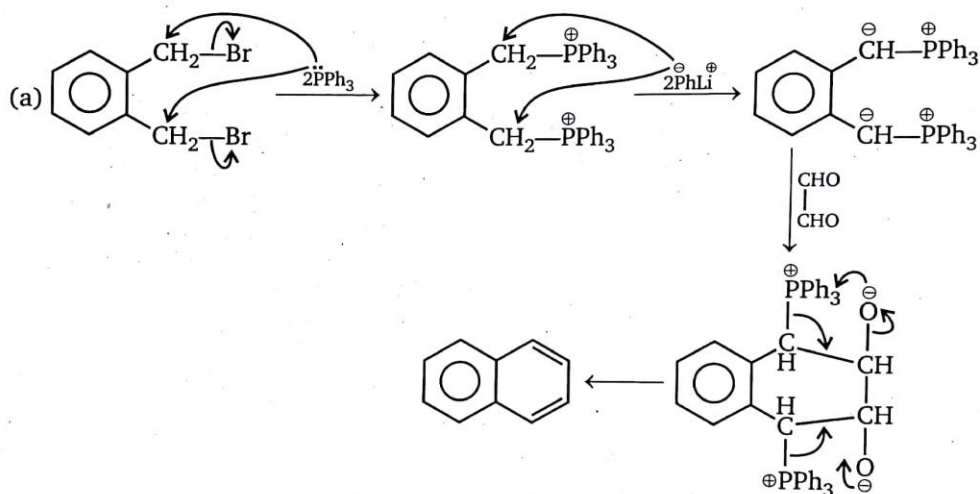
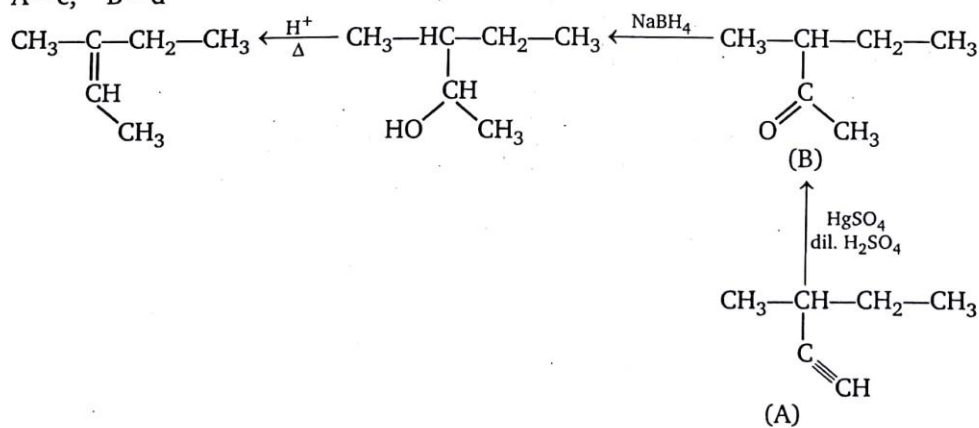
13. A – c; B – d

$$CH_3-\underset{\underset{CH-CH_3}{\|}}{C}-CH_2-CH_3 \xleftarrow[\Delta]{H^+} CH_3-\underset{\underset{HO\ \ CH_3}{CH}}{HC}-CH_2-CH_3 \xleftarrow{NaBH_4} CH_3-\underset{\underset{O\ \ \ CH_3}{C}}{CH}-CH_2-CH_3$$

(B)

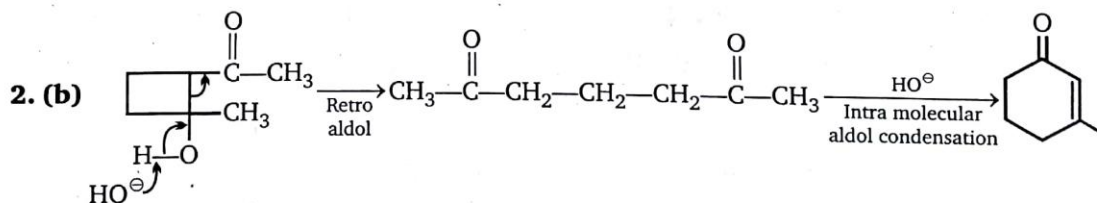
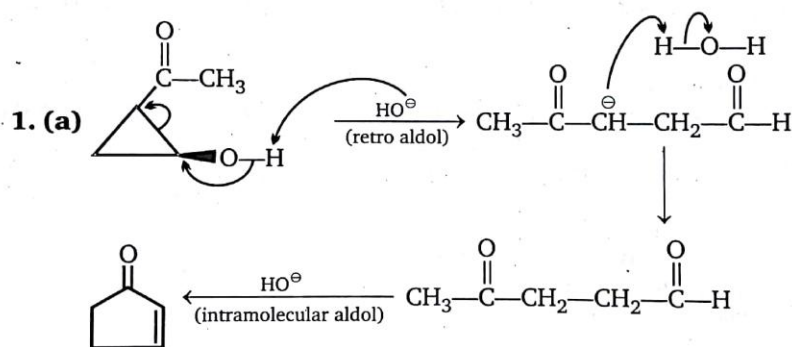
$\uparrow$ $HgSO_4$, dil. H_2SO_4

$$CH_3-\underset{\underset{C\equiv CH}{|}}{CH}-CH_2-CH_3$$

(A)

8 Aldol and Cannizzaro Reaction

Level-1

1. (a) $\xrightarrow[\text{(retro aldol)}]{HO^{\ominus}}$ $CH_3-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{C}H-CH_2-\overset{O}{\overset{\|}{C}}-H$ (H—O—H) $\longrightarrow$ $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-H$ $\xrightarrow[\text{(intramolecular aldol)}]{HO^{\ominus}}$ cyclopentenone

2. (b) $\xrightarrow[\text{aldol}]{\text{Retro}}$ $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$ $\xrightarrow[\text{aldol condensation}]{HO^{\ominus}\ \text{Intra molecular}}$

3. (a) enol will attack a ketone

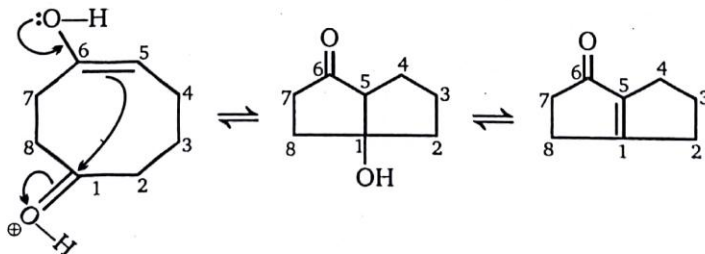
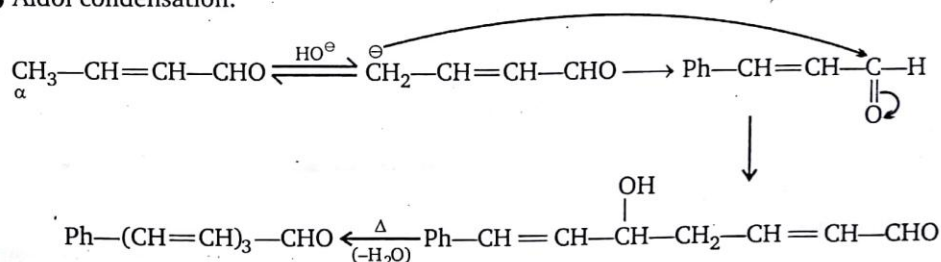
4. (b) Intramolecular aldol condensation.

5. (b) Aldol condensation.

$$\underset{\alpha}{CH_3}—CH=CH—CHO \underset{}{\overset{HO^{\ominus}}{\rightleftharpoons}} \overset{\ominus}{C}H_2—CH=CH—CHO \longrightarrow Ph—CH=CH—\underset{\underset{O}{\|}}{C}—H$$

$$Ph—(CH=CH)_3—CHO \xleftarrow[(-H_2O)]{\Delta} Ph—CH=CH—\underset{OH}{CH}—CH_2—CH=CH—CHO$$

6. (c) $CH_3CHO \xrightarrow{NaOH} CH_3—CH=CH—CHO \xrightarrow{H_2/Ni} CH_3—CH_2—CH_2—CH_2—OH$

7. (b) Intramolecular aldol.

8. (b) Intramolecular aldol reaction.

9. (b) An unsymmetrical ketone such as 2-methylcyclohexanone can form two possible enolates. Just which enolate is formed predominantly depends on the base used and on the conditions employed. The enolate with the more highly substituted double bond is the thermodynamically more stable enolate in the same way that an alkene with the more highly substituted double bond is the more stable alkene. This enolate, called the thermodynamic enolate, is formed predominantly under conditions that permit the establishment of an equilibrium. This will generally be the case if the enolate is produced using a relatively weak base in a protic solvent.

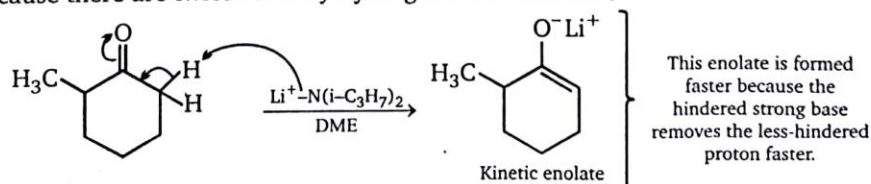
Kinetic (less stable) enolate ⇌ 2-Methylcyclohexanone $\underset{\text{protic solvent}}{\overset{\text{weak base}}{\rightleftharpoons}}$ Thermodynamic (more stable) enolate

This enolate is more stable because the double bond is more highly substituted. It is the predominant enolate present at equilibrium.

On the other hand, the enolate with the less substituted double bond is usually formed faster, because removal of the hydrogen necessary to produce this enolate is less sterically hindered. This enolate, called the kinetic enolate, is formed predominantly when the reaction is kinetically controlled (or rate controlled.)

The kinetically favored enolate can be formed cleanly through the use of lithium diisopropylamide (LDA). This strong, sterically hindered base rapidly removes the proton from the less substituted α carbon of the ketone. The following, using 2-methylcyclohexanone, is an illustration. The solvent for the reaction is 1,2-dimethoxyethane ($CH_3OCH_2CH_2OCH_3$), abbreviated **DME**. The LDA removes the hydrogen from the $—CH_2—$ α carbon more rapidly because it is less hindered (and because there are twice as many hydrogens there to react).

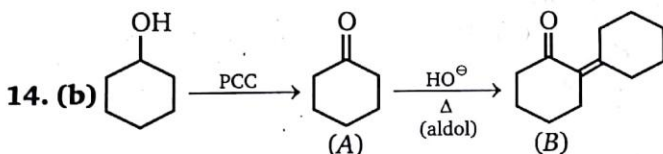
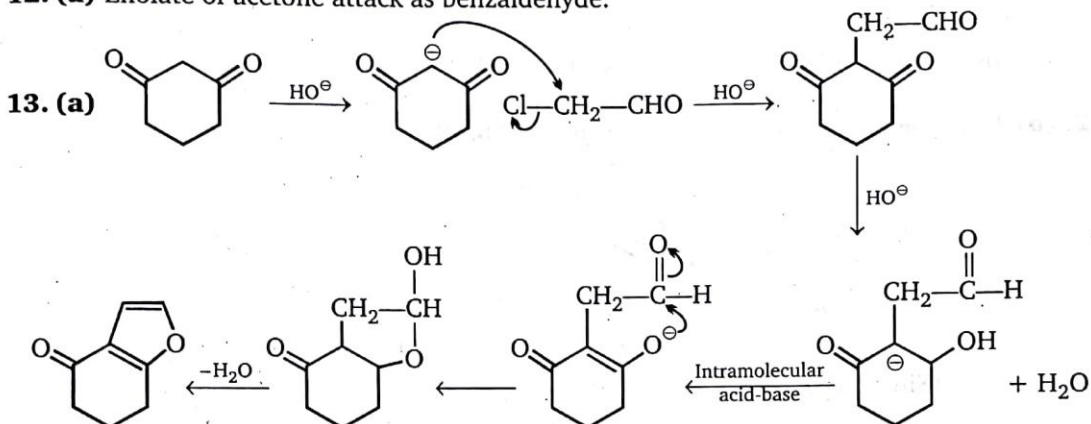
$\xrightarrow[DME]{Li^+ \, ^-N(i-C_3H_7)_2}$ Kinetic enolate (O^-Li^+)

This enolate is formed faster because the hindered strong base removes the less-hindered proton faster.

10. (c) Intramolecular Cannizzaro reaction.

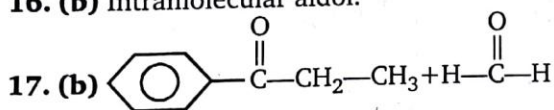
11. (a) $-M$ of two carbonyl group stabilize the carbanion.

12. (a) Enolate of acetone attack as benzaldehyde.

13. (a) Cyclohexane-1,3-dione $\xrightarrow{HO^\ominus}$ enolate (carbanion) + Cl—CH_2—CHO $\xrightarrow{HO^\ominus}$ 2-(CH_2—CHO)-cyclohexane-1,3-dione $\xrightarrow{HO^\ominus}$ carbanion with CH_2—C(=O)—H, OH + H_2O $\xrightarrow{\text{Intramolecular acid-base}}$ enolate ($O^\ominus$) with CH_2—C(=O)—H $\longrightarrow$ cyclic hemiacetal (CH_2—CH(OH)—O) $\xrightarrow{-H_2O}$ furan-fused cyclohexanone

14. (b) Cyclohexanol $\xrightarrow{PCC}$ Cyclohexanone (*A*) $\xrightarrow[\Delta \text{ (aldol)}]{HO^\ominus}$ 2-cyclohexylidenecyclohexanone (*B*)

15. (a) In presence of NaOH intramolecular aldol condensation take place.

16. (b) Intramolecular aldol.

17. (b) C_6H_5—C(=O)—CH_2—CH_3 + H—C(=O)—H

Formaldehyde is highly reactive toward nucleophilic attack.

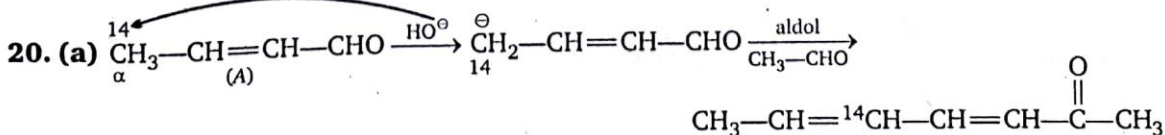
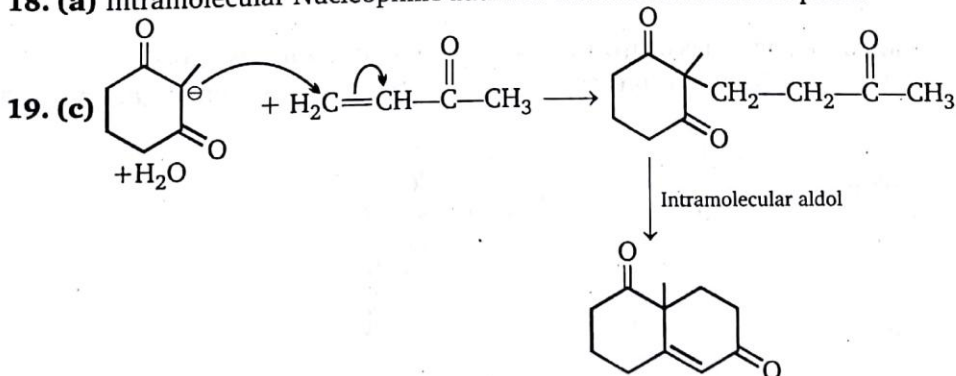
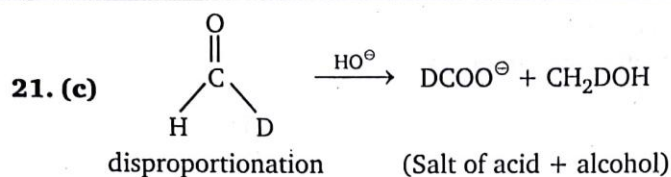
18. (a) Intramolecular Nucleophilic addition-elimination reaction place.

19. (c) 2-methylcyclohexane-1,3-dione carbanion + H_2O + H_2C=CH—C(=O)—CH_3 $\longrightarrow$ 2-methyl-2-(CH_2—CH_2—C(=O)—CH_3)-cyclohexane-1,3-dione $\xrightarrow{\text{Intramolecular aldol}}$ bicyclic enone (Wieland–Miescher type ketone)

20. (a) $\overset{14}{C}H_3$—CH=CH—CHO (*A*) (α) $\xrightarrow{HO^\ominus}$ $\overset{\ominus}{C}H_2$—CH=CH—CHO (14) $\xrightarrow[CH_3—CHO]{\text{aldol}}$

CH_3—CH=^{14}CH—CH=CH—C(=O)—CH_3

21. (c) H–C(=O)–D $\xrightarrow{HO^{\ominus}}$ $DCOO^{\ominus} + CH_2DOH$

disproportionation (Salt of acid + alcohol)

22. (b) Aldehyde gives positive test with Tollen's reagent.

$C_9H_{10}O \xrightarrow[KMnO_4]{[O]}$ (benzene-1,2-dicarboxylic acid: COOH, COOH)

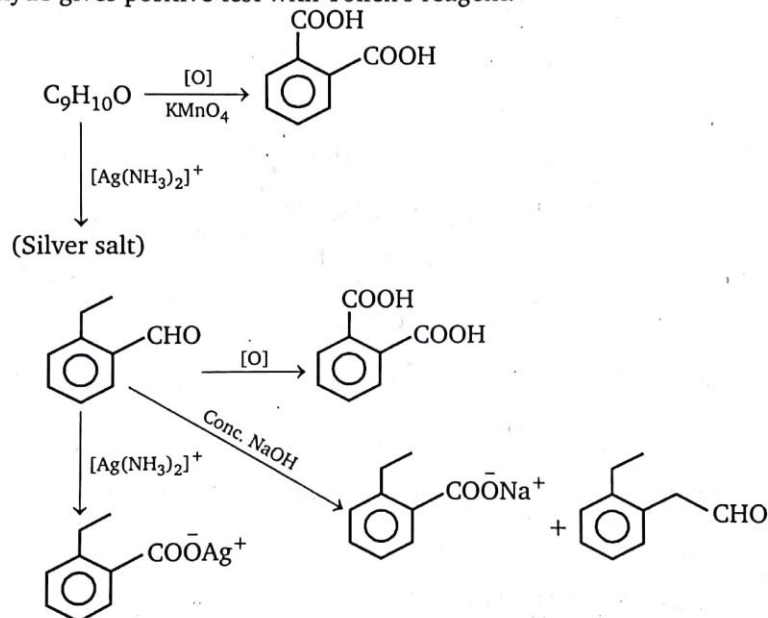
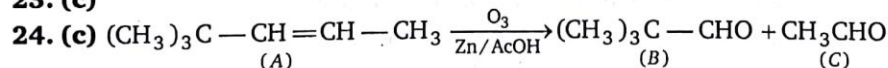
$C_9H_{10}O \xrightarrow{[Ag(NH_3)_2]^+}$ (Silver salt)

2-Ethylbenzaldehyde (CHO) $\xrightarrow{[O]}$ (benzene-1,2-dicarboxylic acid: COOH, COOH)

2-Ethylbenzaldehyde $\xrightarrow{[Ag(NH_3)_2]^+}$ $C_6H_4(C_2H_5)COO^-Ag^+$

2-Ethylbenzaldehyde $\xrightarrow{Conc.\ NaOH}$ $C_6H_4(C_2H_5)COO^-Na^+$ + $C_6H_4(C_2H_5)CH_2$ CHO

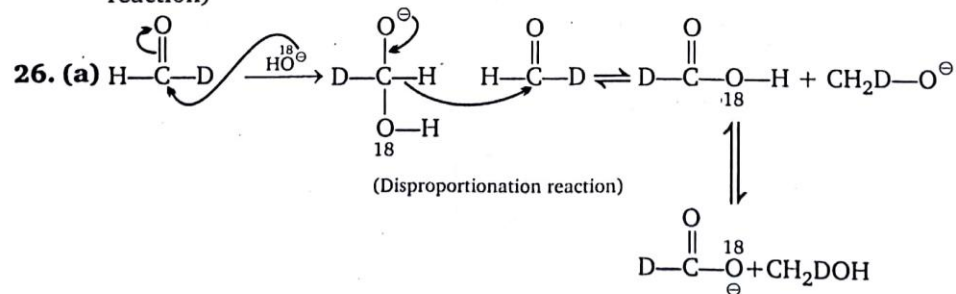
23. (c)

24. (c) $\underset{(A)}{(CH_3)_3C-CH=CH-CH_3} \xrightarrow[Zn/AcOH]{O_3} \underset{(B)}{(CH_3)_3C-CHO} + \underset{(C)}{CH_3CHO}$

25. (d) (c) Exception although it has α-hydrogen it undergo Cannizzaro reaction.

(d) $Ph-CH_2-CHO$ (due to presence of α-hydrogen it will not under go Cannizzaro reaction)

26. (a) H–C(=O)–D $\xrightarrow{H^{18}O^{\ominus}}$ D–C(O$^{\ominus}$)(H)–^{18}O–H + H–C(=O)–D $\rightleftharpoons$ D–C(=O)–^{18}O–H + $CH_2D-O^{\ominus}$

(Disproportionation reaction)

$\rightleftharpoons$ D–C(=O)–^{18}O$^{\ominus}$ + CH_2DOH

27. (c) Michael addition + Intramolecular aldol.

28. (b) Salicylaldehyde $\xrightarrow[\text{Perkin reaction}]{Ac_2O,\ AcONa}$ [intermediate] $\xrightarrow{-H_2O}$ Coumarin

29. (c) $\xrightleftharpoons{HO^\ominus}$ ... $\xrightleftharpoons[\text{acid-base reaction}]{\text{Intra-molecular}}$

intra aldol

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-Et \rightleftharpoons H-O-H + \overset{\ominus}{C}H_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-Et$$

30. (c) (*A*) CH_3CHO (*B*) $HO-CH_2-\underset{CH_2-OH}{\overset{CH_2-OH}{C}}-CHO$ (By cross aldol)

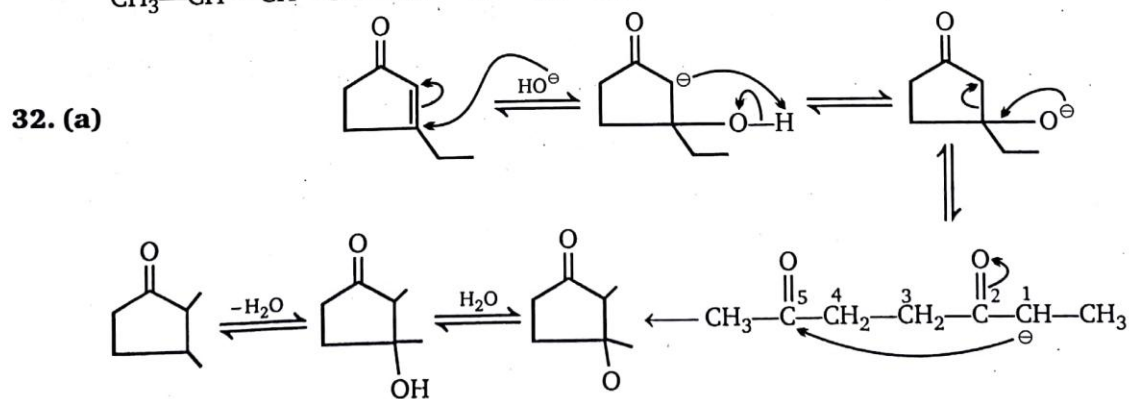
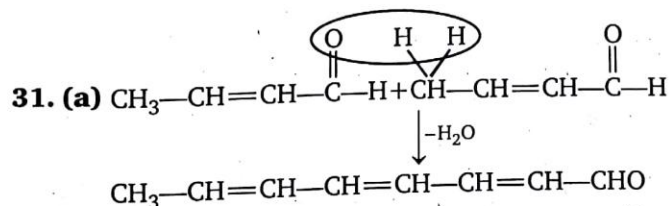
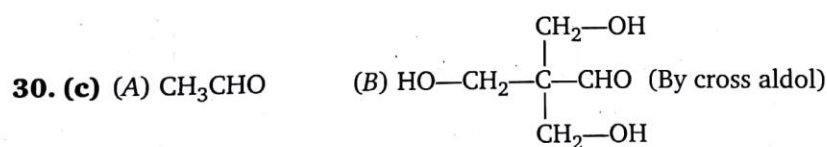
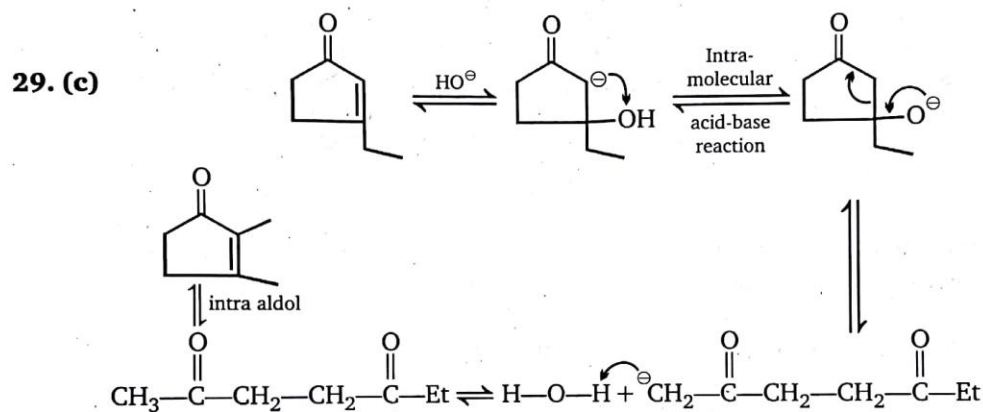
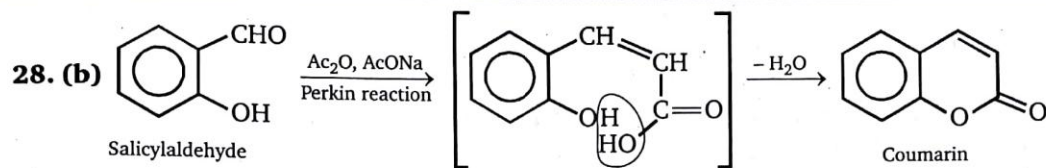
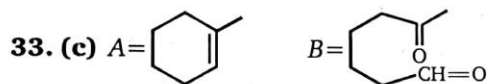
31. (a) $CH_3-CH=CH-\overset{O}{\overset{\|}{C}}-H + CH_2-CH=CH-\overset{O}{\overset{\|}{C}}-H$

$\downarrow -H_2O$

$CH_3-CH=CH-CH=CH-CH=CH-CHO$

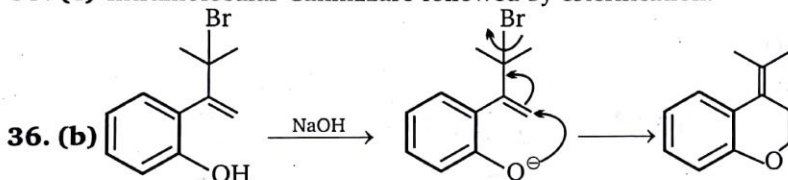
32. (a) $\xrightleftharpoons{HO^\ominus}$ ... $\rightleftharpoons$ ...

$\xleftharpoons{-H_2O}$ ... $\xleftharpoons{H_2O}$ ... $\longleftarrow CH_3-\overset{O}{\overset{\|}{C}}_5-\overset{4}{C}H_2-\overset{3}{C}H_2-\overset{O}{\overset{\|}{C}}_2-\overset{1}{\overset{\ominus}{C}}H-CH_3$

33. (c) $A=$ $B=$ CH=O

It undergoes intramolecular aldol condensation.

34. (a) Intermolecular Aldol condensation.

35. (c) Intramolecular Cannizzaro followed by esterification.

36. (b) Br, OH $\xrightarrow{NaOH}$ Br, $O^{\ominus}$ $\longrightarrow$ O

37. (b)

38. (b) Cross Cannizzaro reaction.

39. (c) (c) is cross aldol product.

40. (b, c)

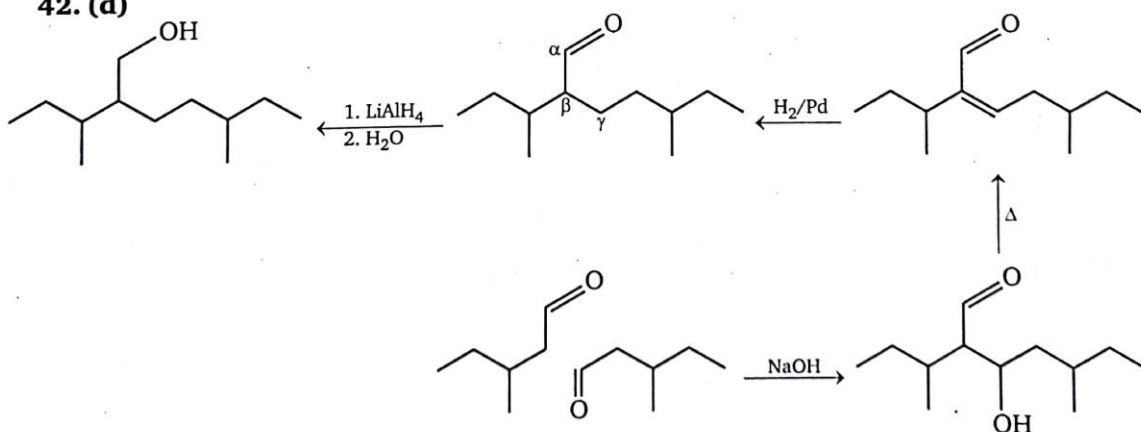
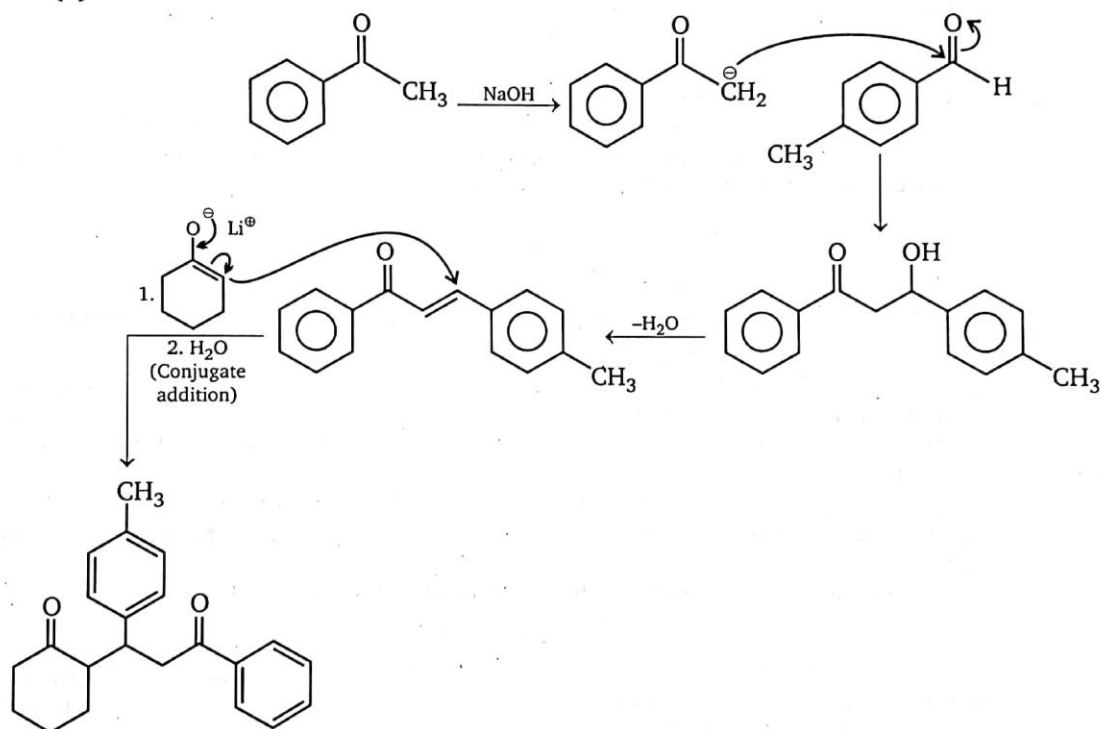
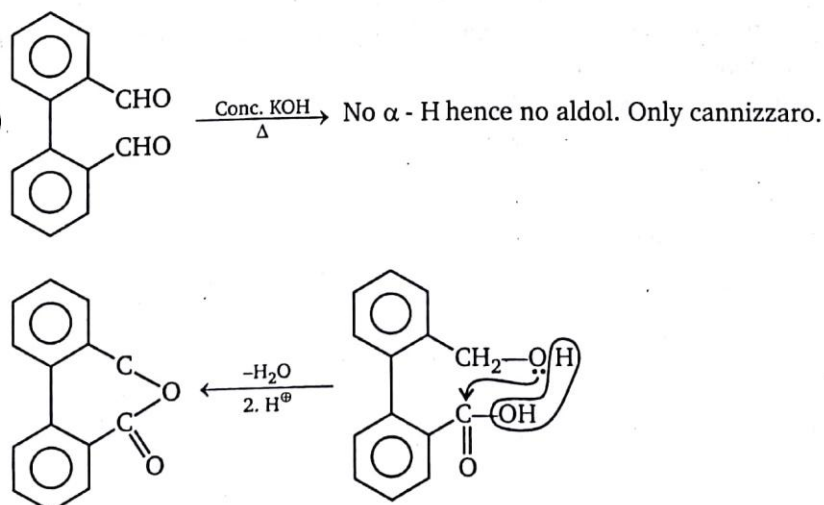
2(b & c) (Due to electron donating group)

41. (d)

42. (d)

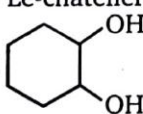
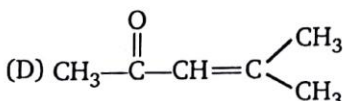
OH $\xleftarrow[2.\ H_2O]{1.\ LiAlH_4}$ O, α, β, γ $\xleftarrow{H_2/Pd}$ O

$\uparrow \Delta$

O, O $\xrightarrow{NaOH}$ O, OH

Level-2

1. This involves hydride transfer from an aldehyde molecule lacking a-H atom, *e.g.*, HCHO, $R_3\dot{C}CHO$, ArCHO, to a second molecule of either the same aldehyde (disproportionation) or sometimes to a molecule of a different aldehyde ('crossed' Cannizzaro). The reaction requires the presence of strong bases, and with, for example, PhCHO the rate law is found to be,

$$\text{Rate} = k[\text{PhCHO}]^2[^{\ominus}\text{OH}]$$

and the reaction is believed to follow the pathway :

Rapid, reversible addition of $^{\ominus}$OH to PhCHO yields the potential hydride donor, this is followed by slow, rate-limiting hydride transfer to the carbonyl carbon atom of a second molecule of PhCHO, and the reaction is completed by rapid proton exchange to yield the more stable pair. Mutual oxidation/reduction of two molecules of aldehyde has thus taken place to yield one molecule each of the corresponding carboxylate anion of the primary alcohol.

Suitable dialdehydes can also undergo intramolecular hydride transfer, as in the Cannizzaro reaction of ethan-1, 2-dial (glyoxal') → hydroxyethanoate ('glycollate,') anion,

for which the observed rate law is found, as expected, to be :

$$\text{Rate} = k[\text{OHCCHO}][^{\ominus}\text{OH}]$$

Aldehydes that possess H atoms on the carbon atom adjacent to the CHO group (the α-carbon atom) do not undergo the Cannizzaro reaction with base, as they undergo the Aldol reaction very much faster.

2. a – Donar = C, Acceptor = C ; b – Donar = E, Acceptor = D ;

c – Donar = B , Acceptor = A ; d – Donar = G, Acceptor = G ; e – Donar = F, Acceptor = Bs

3. (A) Aldol ⟶ Aldol condensation

mol. wt = x mol. wt = $2x - 2$

∴ β-hydroxy ketone = $2x = 144 \Rightarrow x = 72$

(B) Le-chatelier's principle

(C) cyclohexane-1,2-diol (OH, OH) (mol. mass = 116)

(D) $CH_3-\overset{O}{\overset{\|}{C}}-CH=C(CH_3)_2$ given test for alkene.

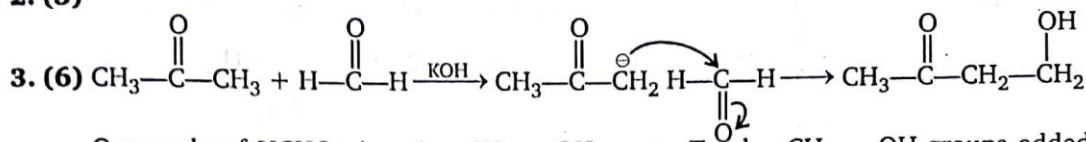
(E) Methyl ketone give positive haloform reaction.

4. A – b, B – b, C – c

SUBJECTIVE PROBLEMS

1. (6) $X = 5$ (B, D, G, H, J) (β-hydroxy carbonyl is aldol product).
$Y = 1$ (I) (stronger acid than H_2CO_3)

2. (3)

3. (6) $CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + H-\overset{O}{\overset{\|}{C}}-H \xrightarrow{KOH} CH_3-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{C}H_2\ H-\underset{\underset{O}{\|}}{C}-H \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{OH}{\overset{|}{C}H_2}$

One mole of HCHO gives 1 $-CH_2-OH$ group. Total $-CH_2-OH$ groups added in product = 6

Hence moles of HCHO consumed = 6.

4. (9)

$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{KOH} CH_3-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{C}H_2\quad CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

$\downarrow$

$CH_3-\overset{O}{\overset{\|}{C}}-CH=\underset{\underset{CH_3}{|}}{C}-CH_2-CH_3 \xleftarrow{\Delta} CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\underset{\underset{CH_3}{|}}{\overset{OH}{\overset{|}{C}}}-CH_2-CH_3$

(2 products. G.I.)

$CH_3-\overset{O}{\overset{\|}{C}}-CH_3+CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{KOH} CH_3-\overset{O}{\overset{\|}{C}}-CH_3\quad CH_3-CH_2-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{C}H_2$

$\downarrow$

$(CH_3)_2C=CH-\overset{O}{\overset{\|}{C}}-CH_2-CH_3 \xleftarrow{\Delta} CH_3-\underset{\underset{CH_3}{|}}{\overset{OH}{\overset{|}{C}}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$

(1 product)

$CH_3-\overset{O}{\overset{\|}{C}}-CH_3+CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{KOH} CH_3-\overset{O}{\overset{\|}{C}}-CH_3\quad CH_3-\overset{\ominus}{C}H-\overset{O}{\overset{\|}{C}}-CH_3$

$\downarrow$

$(CH_3)_2C=C(CH_3)-\overset{O}{\overset{\|}{C}}-CH_3 \xleftarrow{\Delta} CH_3-\underset{\underset{CH_3}{|}}{\overset{OH}{\overset{|}{C}}}-\underset{\underset{CH_3}{|}}{\overset{H}{\overset{|}{C}}}-\overset{O}{\overset{\|}{C}}-CH_3$

(1 product)

$$CH_3-\overset{O}{\overset{||}{C}}-CH_3 + CH_3-\overset{O}{\overset{||}{C}}-CH_3 \xrightarrow{KOH} CH_3-\overset{O}{\overset{||}{C}}-\overset{\ominus}{C}H_2 \quad CH_3-\overset{O}{\overset{||}{C}}-CH_3$$

$$\downarrow$$

$$CH_3-\overset{O}{\overset{||}{C}}-CH=C(CH_3)_2 \xleftarrow{\Delta} CH_3-\overset{O}{\overset{||}{C}}-CH_2-\overset{OH}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3$$

(1 product)

$$CH_3-\overset{O}{\overset{||}{C}}-CH_2-CH_3 + CH_3-\overset{O}{\overset{||}{C}}-CH_2-CH_3 \xrightarrow{KOH} CH_3-\overset{O}{\overset{||}{C}}-\overset{\ominus}{C}H-CH_3 \quad CH_3-\overset{O}{\overset{||}{C}}-CH_2-CH_3$$

$$\downarrow$$

$$CH_3-\overset{O}{\overset{||}{C}}-\underset{CH_3}{\underset{|}{C}}=C\begin{matrix} CH_2-CH_3 \\ CH_3 \end{matrix} \xleftarrow{\Delta} CH_3-\overset{O}{\overset{||}{C}}-\underset{CH_3}{\underset{|}{CH}}-\overset{OH}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2-CH_3$$

(2 products, Geometrical isomers)

$$CH_3-\overset{O}{\overset{||}{C}}-CH_2-CH_3 + CH_3-\overset{O}{\overset{||}{C}}-CH_2-CH_3 \xrightarrow{KOH} \overset{\ominus}{C}H_2-\overset{O}{\overset{||}{C}}-CH_2-CH_3 \quad CH_3-\overset{O}{\overset{||}{C}}-CH_2-CH_3$$

$$\downarrow$$

$$CH_3-CH_2-\overset{O}{\overset{||}{C}}-CH=C\begin{matrix} CH_2-CH_3 \\ CH_3 \end{matrix} \xleftarrow{\Delta} CH_3-CH_2-\overset{O}{\overset{||}{C}}-CH_2-\overset{OH}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2-CH_3$$

(2 products Geometrical isomers)

Total products = 2 + 1 + 1 + 1 + 2 + 2 = 9